Weeds

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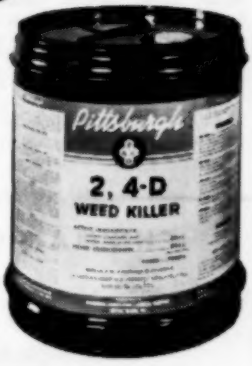

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Weeds

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VOLUME II JANUARY 1953 NUMBER 1

Herbicidal Tests for Control of Para Grass on Ditch Banks in the Everglades Region of Florida[1]

WILLIAM H. SPEIR[2] and JOHN C. STEPHENS[3]

SUB-TROPICAL climate and rich organic soils in the Florida Everglades produce rank growths of vegetation in ditches and on their banks. This causes some of the most troublesome problems encountered in the field of water control. The regular cleaning of such channels to allow designed flow presents a costly problem to farmers and drainage districts.

WEED PROBLEMS IN EVERGLADES DRAINS

Three types of weeds present the principal problems in maintaining canals and ditches in this area. These are the floating aquatics, the submerged aquatics, and the perennial grasses which grow along the ditchbanks and extend into the stream.

Prior to 1946, (1, 2, 3) the water hyacinth *(Eichhornia crassipes)*, a floating water plant whose luxuriant growth had completely covered most of the major canals and farm ditches of the Everglades area, was the major contributor to the inefficiency of drainage canals. Since this initial eradication, the hyacinth problem in the District's canals has been controlled by a routine patrol program using 2,4–D spray for killing new growth which may drift from untreated laterals.

Another group of weeds, the submerged aquatics of which *Najas guadelupensis* is the worst offender, presents a problem similar to that of hyacinths, and equally as hard to combat mechanically. When water hyacinths were eradicated, it was discovered that these submerged aquatics were replacing the hyacinths in canals and ditches of moderate depth where the hyacinths had formerly excluded light necessary for submerged growths.

A paper describing the promising results obtained by the use of WS–1492, an aromatic oil of petroleum origin, was issued (4) in 1951. However, the National Defense Program has prevented the manufacture of this product and experiments are being continued to find a suitable product to control the submerged aquatics.

[1]Florida Agricultural Experiment Station Journal Series, No. 96.

[2]Technical Aide (Hydraulic), Soil Conservation Service.

[3]Research Project Supervisor, Soil Conservation Service and Drainage Engineer, Everglades Experiment Station.

A third group contributing to ditch maintenance problems is comprised of the perennial hydrophytic grasses, which are not strictly aquatic but whose root systems are established along ditch banks and below the water line paralleling the edges of drainage channels. Their rank growth produces a dense mass of runners extending into the channel, which not only reduces its cross-sectional area and raises the retardance coefficient, but also catches debris and entangles aquatic growth making mechanical cleaning unusually difficult.

Para grass *(Panicum barbinode)* is currently the worst offender in this category throughout the Everglades region. As mechanical means of removal are costly and produce little lasting effect in combating the encroachment of this grass, a study of the practicability of the use of herbicides as an agent in control of this pest was made during the past year by the Division of Drainage and Water Control of the Soil Conservation Service in cooperation with the Central and Southern Florida Flood Control District and the Florida Agricultural Experiment Station.

FIELD TESTS FOR CONTROL OF PARA GRASS

Location and Layout of Plots:

Just west of Fla. State Road 7, a stretch along Cypress Creek Canal, was selected as the site for the field tests. This stretch is approximately one and one-half miles long and was heavily infested with para grass, both in the channel and across the surface of the sandy spoil bank.

In the trials, 16 treatments using various herbicides at different rates and in combination with added adjuvants were used. Each of the 16 different treatments was applied in triplicate for replication purposes to offset unforeseen factors that might occur under field conditions, and to provide a means of averaging results for a more accurate analysis.

Forty-eight plots were laid out for treatment and numbered successively 1 through 48. Each plot was 100 feet in length parallel to the spoil bank and extended 35 feet from the water's edge laterally across the slope and crest of the spoil bank. Balks 50 feet long (to remain untreated) were left between plots to serve as checks and to prevent possible contamination of adjoining plots by wind action.

For randomization, the 48 test plots were divided into three blocks. Each block being comprised of 16 plots. The "A" block of plots was laid out consecutively. The "B" and "C" blocks were scattered as to sequence throughout the remaining 32 plots, thus randomizing all blocks.

Formulation and Application of Treatments:

The 16 different herbicidal treatments were mixed and applied on a per acre basis, as shown below. Since each plot contained .08 of an acre, the actual quantities applied were approximately one-twelfth of these amounts. Many of the materials were furnished gratis by chemical companies[4] and others were purchased locally.

[4]Acknowledgment is made for certain experimental materials supplied by Dow Chemical Co., DuPont Co., Monsanto Chemical Co., and Pacific Coast Borax Co.

Treatment 1: 150 lbs. 90% Sodium TCA (Dow) in 150 gals. H_2O. Applied in one application.

Treatment 2: 125 lbs. 90% Sodium TCA (Geigy) in 250 gals. H_2O. Applied in one application.

Treatment 3: 100 lbs. 90% Sodium TCA (Dow) in 100 gals. H_2O. Applied in one application.

Treatment 4: 60 lbs. 90% Sodium TCA (Geigy) plus 15 gals. Shell Weed Killer 130, mixed in 120 gals. of water. Applied in one application.

Treatment 5: Eleven and one-fourth gals. of Isopropyl TCA (Monsanto) and one pint Triton emulsifier in 125 gals. H_2O. Applied in one application.

Treatment 6: 125 lbs. 90% Sodium TCA (Geigy) plus 19 ozs. Dreft detergent for spreader, added to 125 gals. H_2O. Applied in one application.

Treatment 7: 15 gals. Shell Weed Killer 130 in 110 gals. H_2O at first application, followed 6 weeks later by 412 lbs. Polybor-Chlorate-88 in 315 gals. H_2O.

Treatment 8: 25 lbs. 90% Sodium TCA (Geigy) in 125 gals. H_2O applied at first application, followed at three weeks and six weeks later with same application.

Treatment 9: 825 lbs. of Polybor-Chlorate-88 in 625 gals. H_2O. Applied in one application.

Treatment 10: 125 lbs. 90% Sodium TCA (Geigy) plus 2½ gals. of kerosene and ¾ pint of Triton emulsifier in 125 gals. H_2O. Applied in one application.

Treatment 11: 125 lbs. 90% Sodium TCA (Geigy) plus 2½ gals. Xylol and ¾ pint of Triton emulsifier in 125 gals. of H_2O. Applied in one application.

Treatment 12: 15 gals. Shell Weed Killer 130 in 110 gals. H_2O applied at first application, followed three weeks later by application of 60 lbs. 90% Sodium TCA (Monsanto) in 60 gals. H_2O.

Treatment 13: 125 lbs. 90% Sodium TCA (Dow) in 125 gals. H_2O. Applied in one application.

Treatment 14: 125 lbs. 90% Sodium TCA (Monsanto) in 125 gals. H_2O. Applied in one application.

Treatment 15: 125 lbs. 90% Calcium TCA (Dow) in 125 gals. H_2O. Applied in one application.

Treatment 16: 80 lbs. 80% CMU Weed Killer (DuPont) in 160 gals. H_2O. Applied in one application.

A commercial spraying company was hired by the Flood Control District to apply the herbicides under the supervision of Soil Conservation Service research personnel. Approach roads were built to the crest of the spoil bank of the canal to facilitate use of spraying

equipment. Fallen trees and debris along the crest of the bank that would interfere with movement of spray equipment was removed, while due care was exercised to leave the para grass as undisturbed as possible. Spraying was done with a high pressure pump mounted on a Willys ¼ ton Jeep equipped with a 50-gallon spray tank. All herbicidal mixtures were kept well agitated and applied as uniformly as possible over each plot through an adjustable spray nozzle at pressures ranging from 300 to 400 p.s.i. Due to the steepness of the canal banks and the roughness of the terrain, it was not possible for the operators to obtain absolutely uniform distribution of the spray over each plot; however, since the applications were made by experienced commercial operators, the density of application was probably more uniform than would be obtained on regular farm jobs.

Rainfall and Soil Moisture Conditions:

Since the effectiveness of several of the soil sterilizing agents used are adversely affected by lack of sufficient rainfall to carry the material down into the root zone of the soil, a recording rain gage was installed prior to spraying operations. A complete record of rainfall before, during and after treatment was obtained to observe its influence on the treatments.

Initial spray applications were made from July 18th through the 24th during which time 3.05 inches of rain fell. The week prior to spraying, 1.4 inches of rain had fallen, and the week after spraying, 2.54 inches occurred. Rainfall during the following months was: August, 4.08 inches; September, 3.80 inches, and November, 13.50 inches. Thus, sufficient rain fell to carry the sprays well into the root zone. In fact, because of the permeable nature of the deep sandy soil, it is likely that some of the herbicides were leached from the soil too soon for maximum residual effect.

METHOD OF EVALUATING PLOT KILLS

Observation:

These tests were planned to study herbicidal qualities of the treatments when done under field conditions, and the test plots used were quite large. The experiment covered a long strip of canal bank so rough that it was not considered feasible to make survival counts such as are made on smaller experimental plots where the initial weed coverage is uniform.

In the field the degree of kill was determined by observing and comparing the treated plots against the untreated checks and against the other treatments. The precision of accuracy thus depended largely upon the observation and experience of the individual making the inspection, and the personal element was a factor which had to be considered. To reduce the personal error to a minimum, three persons made separate ratings on each plot. Two of the ratings were on a comparative and one on a percent-kill basis. With the comparative ratings, results which achieved complete eradication above the water line were judged as "Excellent", and those treatments that produced little apparent results rated as "Poor", with intermediate listings of "Very Good", "Good", and "Fair".

Tabulation:

A consensus rating was made from the three separate observations on each plot after inspection. The consensus ratings for the "A", "B" and "C" blocks were then averaged to give the results for each of the different treatments. To show the relative effectiveness of the 16 different treatments on a graphical and statistical basis, a numerical system was utilized. "Excellent" (E) was given a numerical rating of 5; "Very Good" (VG) 4; "Good" (G) 3; "Fair" (F) 2; and "Poor" (P) 1. In averaging the individual ratings of each plot, "+" and "—" ratings were assigned to intermediate averages. For example, G— was given the value of 2.75, while G+ was valued at 3.25, with similar bracket values for the other ratings.

A graph was prepared to show the relative kill for each treatment in decreasing order. A statistical analysis was made of the data and by analysis of variance the lowest significant difference at the 5% level was determined. This value was found to be 0.91 and has been plotted to scale on the graph.

RESULTS

Periodic observations following treatment showed a quick blistering or burning effect on those plots treated with the contact killer, Shell 130. The soil sterilizing agents showed slower reactions whose effect became more apparent as time passed.

Past experience indicated that three months should elapse after treatment before valid results would be obtained on complete kills including the root systems. This was borne out by these tests. An inspection made after an interval of six weeks indicated apparent kills which were not validated by later observations. At three months, some of the plots which had shown a severe burn and defoliation at six weeks, had recovered and new growth begun. However, on those plots where the herbicides were more effective, the para grass was dead and both surface growth and root systems had begun to decompose.

Observations made six months after treatment confirmed results obtained at three months. A check made approximately one year after treatment showed the para grass had regrown over all plots with the exception of the ones treated with CMU, Treatment 16, and those where the sprays had been applied in several applications, Treatments 7, 8 and 12.

The results of the inspection made three months after the first treatment are shown graphically in Fig. 1.

From Fig. 1, the tendency of the treatments to fall into different groups is noted. Treatment 16, a single heavy application of CMU, is outstanding and in a class by itself reaching the E— (4.8) mark. The next group, nos. 7, 12 and 8, are all multiple application treatments and form somewhat of a plateau in the VG— (3.9 to 3.7) range above the others. The remaining treatments, which were all applied in one application, range uniformly down from a grade of F+ to P (2.5 to 1.0).

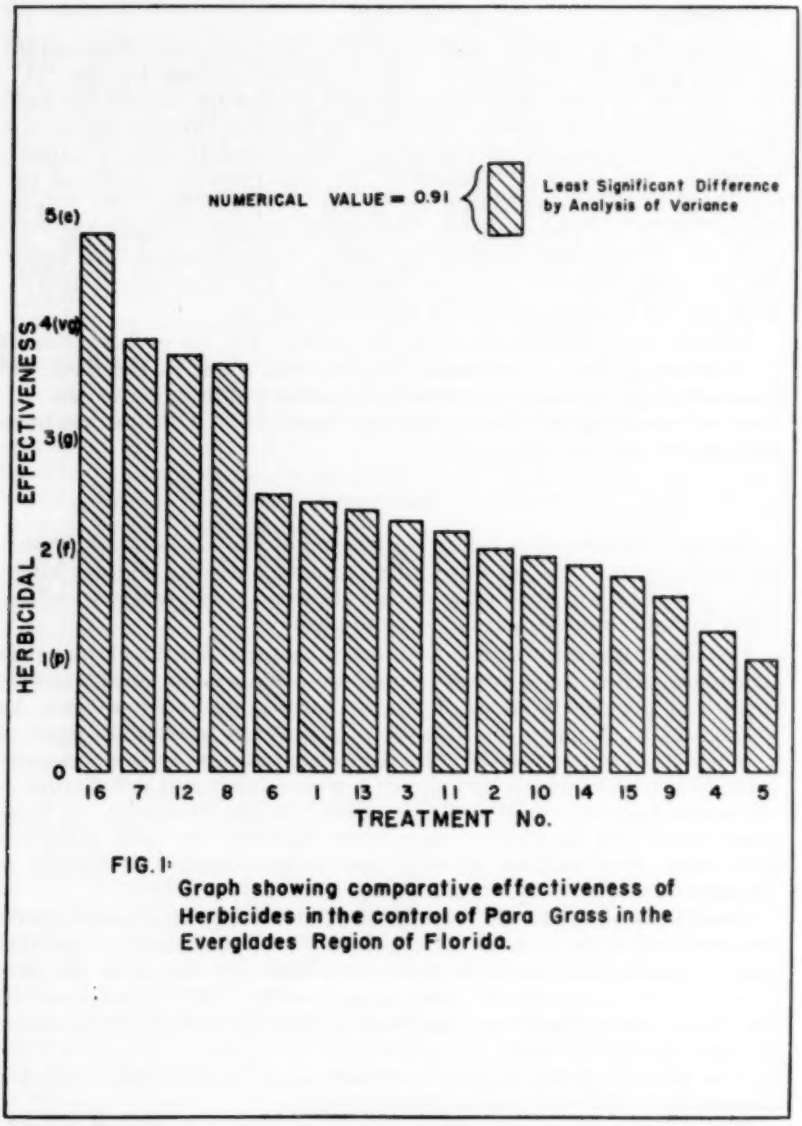

FIG. 1: Graph showing comparative effectiveness of Herbicides in the control of Para Grass in the Everglades Region of Florida.

DISCUSSION

C. M. U.:

It is readily apparent that the CMU Weed Killer (Parachlorophenyl-i, i-dimethylurea) produced the best kill of those herbicides used. An inspection made 6 months after application showed almost no encroachment by the para grass from the untreated balks into the treated plots. Though its present cost may prohibit its general

use for control of para grass on farms, it is thought likely, in view of its complete kill at the rate used, that through the use of the pre-weakening method described below, equally successful results at a smaller application rate might be obtained more economically.

It would have been desirable to have tried CMU at several different rates using both single and multiple applications and in combination with different adjuvants, as was done with Sodium TCA. However, the supply of CMU was obtained after the site had been selected and the plots surveyed so that it was only feasible to include the material at the one relatively heavy rate.

Pre-Weakening Applications:

From Figure 1 the superiority of a group of similar treatments, i.e., nos. 7, 12 and 8, over the remaining treatments is evident. The treatments for this group are all characterized by the initial use of a contact herbicide or a small application of TCA to first weaken the plant, being followed from three to six weeks later with a relatively light application of a soil sterilizing agent.

In Treatment 9, Polybor-Chlorate-88, applied in one application at the rate of 825 lbs. per acre, showed negligible results. However, in Treatment 7, this herbicide produced very good results when applied at the rate of 412 lbs. per acre following pre-treatment with Shell Weed Killer 130. A comparison of Treatment 4 with Treatment 12 will further show the effect of follow-up applications. In no. 4, 90% Sodium TCA, at the rate of 60 lbs. per acre mixed with Shell Weed Killer 130 (15 gals. per acre) and applied at a single application had little effect, while in no. 12, the same amount of TCA produced very good kills when preceded by treatment with Shell Weed Killer 130. Treatment 12, using only 60 lbs. of TCA, produced better results than any of the single treatments using TCA applied at much higher rates.

Small amounts of 90% Sodium TCA used in repeated treatments produced better results than one application of the same chemical at higher rates, as shown by Treatment 8.

A report on the control of ditchbank weeds in California (5) indicate that merely searing the green vegetation with a hot flame kills many plant cells which, in dying, release toxic substances that injure all tissues above ground. Baldwin (6) reports that 500 lbs. of 90% Sodium TCA, 625 lbs. of Ammate, and 1400 lbs. of Polybor-Chlorate per acre, failed to secure 100% eradication of Buttonbush at the Savannah Wildlife Refuge; whereas, at the Santee Refuge, fire-damaged bushes on drained plots succumbed to 110 lbs. of TCA (per acre) and 435 lbs. of Polybor-Chlorate. These results indicate the effectiveness of the pre-weakening principle.

The probability that the initial applications set up toxic reactions within the plant, and injure it to the extent that it is much more susceptible to destruction by later application of the soil sterilizing agents is strongly suggested. Since the cost of materials for the initial pre-weakening treatments is ordinarily much less than that

for the soil sterilizing agents, the savings by this method, where the cost of labor and equipment for making several applications is not too great, is apparent.

Use of 90% Sodium TCA – Single Application:

The third grouping consists of single-treatment applications of 90% TCA at rates varying from 100 to 150 lbs. per acre. Some of the treatments were formulated with additions of different emulsifiers, spreaders, wetting, and penetrating agents. These treatments produced fair results, and as there was only slight variation in effectiveness of the group, it would seem that the adjuvants had little influence on the chemicals' effectiveness.

Use of 90% Calcium TCA:

The 90% Calcium TCA, used in Treatment 15, was slightly less effective than similar treatments using Sodium TCA. It also appeared to be more corrosive.

Use of Polybor-Chlorate-88; Shell Weed Killer 130 Mixed with Sodium TCA; and Isopropyl TCA:

Only negligible results were obtained for any of this group. In Treatment 9, Polybor-Chlorate-88 was used at only one-half the producer's recommended rate and little effect was noted when applied at a single application. This chemical has proved effective when used at recommended rates on smaller plots in other tests but its use when applied at a single-application for complete eradication of para grass on farm lands may not be economically feasible. However, as shown by the effective results obtained from Treatment 7, it may prove more feasible when used in connection with the pre-weakening method.

In Treatment 4, the unsatisfactory results indicate that Shell Weed Killer 130 and 90% Sodium TCA may not be compatible.

In Treatment 5, Isopropyl TCA had no effect at the rate used.

Future Studies:

Additional tests are being planned for control of weeds on ditchbanks with emphasis on the use of the pre-weakening method. Different herbicides, as well as singeing, will be used to determine the most effective and economical initial treatments. Varying rates of application of the different soil sterilizing agents will be made to establish minimum rates required for follow-up treatments. A cost-efficiency study will be incorporated into the program as a basis for selection of herbicides to be recommended.

SUMMARY

Para grass is one of the principal maintenance problems along drainage ways in the Everglades Area. Treatments using Sodium, calcium, and Isopropyl TCA; Polybor-Chlorate-88; and CMU at different rates and in various combinations were tested as herbicides on replicated field plots of .08 acre along an infested canal bank.

CMU was found best but most expensive for control of the Para

grass. A "pre-weakening" method was developed which promises to reduce the expense of eradicating perennial weeds by soil sterilizing chemicals. This method consists of weakening the plant by first treating it with a relatively cheap contact herbicide, or by flame singeing, which appears to develop a toxicity within the plant that renders it more susceptible to killing by fairly small doses of an agent such as TCA, Polybor-Chlorate or CMU applied from three to six weeks later. In these tests, the use of adjuvants seem to have little effect in insuring kills with TCA.

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The Use of C^{14} in a Study of the Leaching Rate of Isopropyl N-Phenyl Carbamate [1, 2]

A. V. Logan and N. R. Odell, *Dept. of Chemistry*, and
V. H. Freed, *Dept. of Agricultural Chemistry*

The use of Isopropyl N-Phenyl Carbamate (IPC) as a residual pre-emergent herbicide (1, 2, 3, 5) depends on the effective concentration remaining in the soil for a period of time. The effectiveness of such a treatment has been shown to be dependent upon several factors (3, 4, 5).

The distribution of the chemical in the soil horizon undoubtedly plays an important part in the ultimate effectiveness in such a treatment. Earlier qualitative studies (5) have shown that IPC is distributed in the soil horizon under influence of moisture, but the exact location of the maximum concentration was not determined. The use of radioactive IPC, (6) makes possible a faster and more completely quantitative method of determining the retention of IPC in soils after leaching than would be possible with standard procedures. The C^{14} labeled IPC was applied to Chehalis sandy loam soil which had been dried at 100 to 110° C. in several 16 mm. soft glass tubes. It was found necessary after preliminary study to pre-extract the soil with 7 ml. of acetone per gram of soil to remove waxy-like organic matter which interfered with the later combustion. It was also shown in these preliminary tests that the behavior of the pre-extracted soil was not essentially different with respect to adsorption and leaching characteristics than the non-extracted soil. Also in the preliminary studies, an attempt was made to use plastic tubing in place of the soft glass tubing but the polar nature of the plastic tubing brought about strong adsorption of the IPC by the tubing invalidating results obtained in that part of the study.

4.155 mg. of radioactive IPC were dissolved in 4 ml. of acetone. The concentration of radioactivity in this stock solution was determined by oxidizing aliquots by the Van Slyke-Folch (7) method. The radioactive material was recovered as barium carbonate. The suspension was filtered through a sintered glass funnel and the precipitate washed three times with water and once with 95% alcohol and dried overnight at 100 to 110° C. The samples for counting were deposited in a thin layer upon a one-inch diameter copper disk. The radioactivity was determined by the use of a Tracerlab 64 Scaler using a thin mica window (1.7 mg/cm^2). The activity of all samples was corrected to zero thickness. The activity of the IPC was found to be 4.33×10^5 c/m/mg.

The total amount of activity which could be recovered under the conditions of the experiment averaged 80.76% or 4.12×10^5 c/m/mg.

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[2]The work reported here was supported in part with the aid of a grant from the Research Corporation, New York, N. Y.

The data collected in the subsequent work were calculated on this basis.

40 g. samples of pre-extracted 50 mesh screen sifted soil were packed in nine-inch columns of 16 mm. soft glass to a height of 8 inches. The tubes were etched deeply at intervals of one inch to facilitate sectioning for counting after the leaching process had been completed. 0.05 ml. of the acetone solution of radioactive IPC was placed on a circle of filter paper covering the column of soil in each of the tubes. Three groups of five tubes each were subjected to the equivalent of 1, 2, or 3 inches of rainfall respectively and leaching was allowed to occur. After leaching for 24, 48, 72, 96 or 120 hours, the five tubes of each group were sectioned and the soil in each section was extracted with 10 ml. of acetone.

In preliminary trials, an attempt was made to evaporate the acetone and count the IPC directly but it was found that the small amount of IPC in the solution sublimed readily during the drying process and as a consequence most of the activity was lost. The final procedure consisted of reducing the acetone solution of radioactive IPC to a small volume, the residue oxidized and the barium carbonate counted as described above.

The data collected indicate that with the equivalent of one inch of rainfall the bulk of the radioactive material remained within the first inch of soil during the entire observation (Plate 1, Fig. 1). No radioactivity was detectable in the fourth inch of soil until the third day.

When leached with the equivalent of two inches of rainfall, radioactivity in the first inch of soil 24 hours after the water was added was only 20% of the total (Plate 1, Fig. 2). However, at the end of the five day period the activity of the first inch of soil had increased to about 30%. It would seem that the addition of water caused an initial flushing of the IPC to the lower level at the beginning of the experiment but that there was an upward movement of the IPC during the succeeding days in the moist soil. This appears to be consistent with results of field tests where normal applications of IPC are about the limit of its solubility in an acre inch of rainfall. However, residual activity is found in the soil some weeks after the application of IPC even though the area may have been subjected to four, five or more inches of rainfall.

When the equivalent of three inches of rainfall was used for the leaching, data were obtained similar to those in the two-inch equivalent although the depth from which radioactive IPC was recovered was increased to seven inches (Plate 1, Fig. 3).

The extraction of soil with acetone and the method of packing in glass tubes are certainly not exactly the conditions encountered in field work. However, the authors feel that the evidence closely parallels that obtained while running tests under entirely different conditions.

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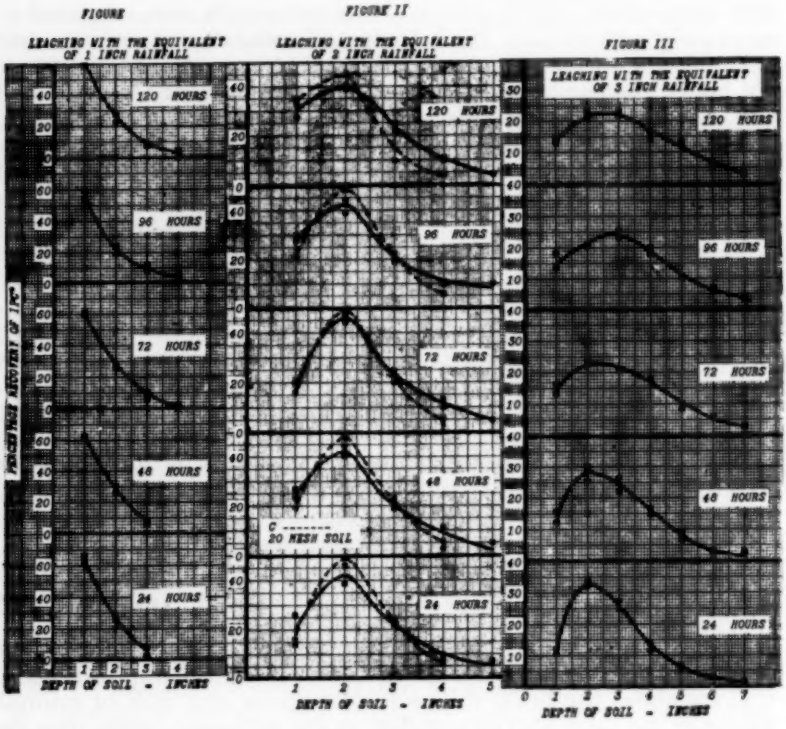

PLATE 1. Figs. 1, 2, and 3. The effect of leaching soil tubes with one, two, and three inches of rainfall equivalent on the percentage recovery of C^{14} labeled IPC.

A Comparison of Five Chemicals for Crabgrass Control[1] in Turf

RALPH E. ENGEL, RICHARD J. ALDRICH and GILBERT H. AHLGREN[2]

CHEMICAL methods offer a quick means of eliminating crabgrass from lawns and other grassed areas. Sodium arsenite, used since 1935 (1), is the oldest of the selective chemical crabgrass killers. In 1947 phenyl mercuric acetate was reported (2) to be effective as a crabgrass killer in the bentgrass type of turf.

In 1948, the New Jersey Agricultural Experiment Station began crabgrass control trials with as many available and promising chemicals as could be obtained. Results from experiments with five of the more effective chemicals are reported here.

MATERIALS AND METHODS

Treatments were made on plots 3 by 10 feet in 1948, and on plots 4 by 15 feet in 1949, 1950 and 1951. All treatments were in triplicate, and the plots were randomized. A one-foot border was left around each plot to separate the plots and give additional information on crabgrass control from the chemical treatments. Check or control plots, however, were standard with all tests.

Initial treatments were made from middle to late August each year. The interval between subsequent treatments was five days in 1948, and seven days in 1949, 1950 and 1951.

The weather was hot and dry in 1948, moderately dry and warm in 1949, cool and moist in 1950, and the temperature was moderate and soil moisture slightly below optimum for turf growth in 1951. These tests were, therefore, conducted under a fairly wide range of climatic and soil moisture conditions.

The tests reported here were conducted on a turf that was primarily Kentucky bluegrass. A small percentage of Chewing's fescue, Colonial bentgrass and *Poa annua* was present but results pertain largely to Kentucky bluegrass. The chemicals tested were potassium cyanate, sodium arsenite, phenyl mercuric acetate, monoammino-boronium fluoride (S–1840),[3] and bis (lauryl, di2–hydroxy–ethyl-ammino) boronium fluoride (S–1998).[4]

The test areas were mowed at a height of 1½ inches in 1948 and 1949, at 1¼ inches in 1950 and at 1 inch in 1951. These differences in height of cut were for convenience in maintenance and, so far as

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[1]Credit is given to Dr. Dale E. Wolf for cooperating in these tests for the years 1948 and 1949 and appreciation is extended to Warren E. Wisendahl for valuable assistance rendered.

[2]Assistant research specialist, Agronomist, USDA, Bureau of Plant Industry, Soils & Agricultural Engineering, Division of Weed Investigations, and Research specialist respectively.

[3]Hereafter referred to as S–1840.

[4]Hereafter referred to as S–1998.

could be determined, had no effect on the crabgrass or bluegrass response to the chemical treatments.

A single nozzle knapsack sprayer was used at a pressure of 15 to 30 pounds per square inch in 1948. In 1949, 1950 and 1951 the chemical solutions were applied through a boom with cone nozzles at pressures of 35 to 40 pounds per square inch. In all cases the chemicals were dissolved in water and the solutions applied at 300 to 700 gallons per acre. The source of chemicals and the concentrations used are given in table 1.

Table 1. Chemicals used in crabgrass control experiments, 1948–1951.

Chemical	Year	Per cent active ingredient	Source
Sodium arsenite	1948	91.0	
Sodium arsenite	1949–51	91.0	
Phenyl mercuric acetate	1948	11.2	Gallowhur Chemical Co.
Phenyl mercuric acetate	1949	11.2	Gallowhur Chemical Co.
Phenyl mercuric acetate	1950	10.4	Cleary Chemical Corp.
Phenyl mercuric acetate	1951	10.0	Cleary Chemical Corp.
S-1840	1948	100.0	Sowa Chemical Co.
S-1840	1949–50	100.0	Sowa Chemical Co.
S-1840M[1]	1951	90.0	Sowa Chemical Co.
S-1998	1948	75.0	Sowa Chemical Co.
S-1998	1949–51	75.0	Sowa Chemical Co.
Potassium cyanate	1948, 1949 & 1951	91.0	American Cyanamid Co.
Potassium cyanate	1950	78.9	American Cyanamid Co.

[1]Modification of S-1840 containing wetting agent and 2,4-D.

The percentage crabgrass control was determined by averaging estimates made independently by three persons in late September of each year except 1950. In that year crabgrass counts were made on four random samples of one square foot each per plot. These have been converted to a percentage basis for convenience in making comparisons. Turf injury ratings were estimated on the basis of 0 = none, 1 = trace, 2 = moderate, 3 = severe, and 4 = very severe. These ratings were made in late September or early October and are an expression of discoloration and thinning of the turf.

RESULTS

Data on the comparative control of crabgrass and on the relative turf injury for the five chemicals reported here are given in tables 2, 3, 4 and 5. The results are reported by years because of some variation due to adjustment of chemical rates and also to seasonal differences in temperature, rainfall, and soil moisture.

In 1948 (table 2) phenyl mercuric acetate, S–1840, S–1998, and potassium cyanate gave significantly better crabgrass control than did sodium arsenite. Phenyl mercuric acetate gave the least turf injury. Turf injury from all treatments was more severe in 1948 than in succeeding years. This is attributed to the hot dry weather at the time of treatment and to early rating of the plots (September 10)

Table 2. Crabgrass control and turf injury resulting from the application of five herbicides, 1948.

Chemical	No. of applications	Lbs. of active ingredient per acre	Gallons of water per acre	Per cent crabgrass control	Turf injury[1]
Sodium arsenite	1	5.45	395	42	3.3
Phenyl mercuric acetate	3	0.92	580	83	2.9
S-1840	1	121.00	726	95	3.4
S-1998	1	135.00	726	81	3.2
Potassium cyanate	1	59.20	484[2]	75	2.9
Potassium cyanate	2	39.90	484[2]	87	3.4
L.S.D. at 19 to 1				25	

[1]Discoloration and thinning of turf rated as follows: 0 = none, 1 = trace, 2 = moderate, 3 = severe and 4 = very severe. This rating applies to all succeeding tables.
[2]0.053% Aersol added as wetting agent.

before the turf had a chance of recovering. Moreover, single heavy applications of S–1840, S–1998 and potassium cyanate were made in 1948. The value of repeated and light applications of these chemicals as a means of reducing turf injury was established in 1949, and this technique was used in subsequent trials.

Better crabgrass control with less turf injury was obtained in 1949 than in the previous year (table 3). It is also evident that sodium arsenite gave the most turf discoloration and the least control in comparison to the other chemicals. Phenyl mercuric acetate gave least turf injury, but only 80 per cent crabgrass control.

Table 3. Crabgrass control and turf injury resulting from the application of five herbicides, 1949.

Chemical	No. of applications	Lbs. of active ingredient per acre	Gallons of water per acre	Per cent crabgrass control	Turf injury
Sodium arsenite	3	2.72	365	74	2.7
Phenyl mercuric acetate	3	0.70	610	80	0.1
S-1840	2	40.00	363	98	1.9
S-1998	3	35.17	363	97	1.8
Potassium cyanate	2	16.00	363[1]	99	1.5
L.S.D. at 19 to 1				13	

[1]0.25% "Vatsol K" wetting agent added.

The 1950 results (table 4) show that excellent crabgrass control was obtained with all materials and that only with sodium arsenite was turf injury of any significance. The crabgrass plants were still small at the time treatment was initiated, and growing conditions for the Kentucky bluegrass were excellent. This probably accounts for the high degree of control with a minimum of turf injury.

In 1951, (table 5) all materials except sodium arsenite again gave satisfactory control of crabgrass. The least turf injury resulted from potassium cyanate; S–1998 and sodium arsenite were intermediate in injury; and phenyl mercuric acetate and S–1840M gave the most injury. These differences probably are not significant.

The four-year average given in table 6 indicates that a high degree of crabgrass control can be obtained by these chemicals with only

Table 4. Crabgrass control and turf injury resulting from the application of five herbicides, 1950.

Chemical	No. of applications[1]	Lbs. of active ingredient per acre	Crabgrass control		Turf injury
			No. plants/ square foot	Per cent	
Sodium arsenite	3	2.5	0.0	100	2.3
Phenyl mercuric acetate	3	0.80	0.2	99	0.2
S-1840	3	20.00	0.0	100	0.5
S-1998	3	35.29	1.5	93	0.7
Potassium cyanate	3	12.00	0.5	98	0.0
Potassium cyanate	3	16.00	0.0	100	0.5
Check	3		22.8		

[1]All applications made in 365 gallons of water per acre.

Table 5. Crabgrass control and turf injury resulting from the application of five herbicides, 1951.

Chemical	No. of applications	Lbs. of active ingredient per acre[1]	Per cent crabgrass control	Turf injury
Sodium arsenite	3	1	68	0.7
Phenyl mercuric acetate	3	0.77	94	1.0
S-1840M	3	20	97	1.7
S-1998	3	22	96	0.7
Potassium cyanate	3	10	92	0.3
L.S.D. at 19 to 1			16	

[1]All applications made in 365 gallons of water per acre; 0.25% "Vatsol K" wetting agent added to potassium cyanate.

slight to moderate injury to the turf. Crabgrass was controlled least effectively by sodium arsenite and in addition turf injury was consistently greater. Differences in crabgrass control and turf injury among the remaining four chemicals were not significant; phenyl mercuric acetate gave the least turf injury and S–1840 the most.

Table 6. Four-year average of crabgrass control and turf injury from five chemicals (1948–1951).

Chemical	Per cent crabgrass control	Turf injury
Sodium arsenite	71	2.25
Phenyl mercuric acetate	89	1.05
S-1840	98	1.88
S-1998	92	1.60
Potassium cyanate	94	1.30

Discussion of Results

In the average of four years tests potassium cyanate, phenyl mercuric acetate, and the two boronium compounds resulted in 89 per cent or better control of crabgrass. Control obtained with sodium arsenite averaged approximately 20 per cent less. Climatic and soil moisture conditions influenced crabgrass control by the chemicals. Generally it appeared that less favorable growing conditions for turf were correlated with less effective crabgrass control.

In interpreting the control results in terms of usage of the chemicals it should be pointed out that the degree of crabgrass control is not necessarily critical in choosing a chemical. The use of sodium arsenite, for example, may be justified where large areas of turf are involved. Frequently complete control is not necessary on such areas and some temporary discoloration is of little consequence.

The value of repeated applications for effective crabgrass control was observed throughout the series of tests. At the rates of application used, effective control with phenyl mercuric acetate was very dependent on repeated applications; in some instances control might have been improved considerably by an additional light application. Usually, the first application of this chemical produced a yellowing of the crabgrass that was intensified by the second application. Little or no kill resulted until the third treatment. All the other chemical treatments gave varying degrees of kill with each application.

Turf injury ratings made 2 to 5 weeks after the last chemical application were largely a measure of injury as expressed by thinning of the turf. The ratings also measured any discoloration which persisted until the plots were rated. Discoloration, which was commonly at a maximum a few days to a week after treatment, was generally of a temporary nature and did not indicate permanent injury of the turf grasses. Observations of treated plots in the present study, and of test plots not reported here, indicated that less favorable growing conditions for turf generally resulted in increased turf injury. Turf injury was least in 1950, when the weather was cool and moist at the time of treatment.

It should be emphasized that the relatively small numerical differences in turf injury among the five chemicals may have considerable practical significance. The lowest average injury rating of 1.05, resulting from phenyl mercuric acetate, represents practically no measurable injury to the turf grasses. The highest average of 2.25, associated with sodium arsenite, represents considerable kill of turf grasses. It should also be pointed out that discoloration, which was not specifically measured in these tests, was observed to be least with phenyl mercuric acetate. Since phenyl mercuric acetate gave generally less turf injury and seemed to kill crabgrass through a cumulative effect, it appears to be superior for early season treatment or for turf areas where discoloration is particularly objectionable.

All of the chemicals used were soluble in water and easily applied as a spray. Since potassium cyanate partly decomposes if left in a water solution, it should be prepared just prior to application. The boronium compounds and potassium cyanate are essentially nonpoisonous and thus offer an advantage over the phenyl mercuric acetate and the sodium arsenite.

Under the conditions of the tests reported here, the range of most effective rates of chemical per acre in each application was 1 to 2 pounds for sodium arsenite; 0.7 to 0.9 pounds for phenyl mercuric acetate; 8 to 16 pounds for potassium cyanate; 20 to 25 pounds for S–1840; and 25 to 30 pounds for S–1998. Climatic and soil conditions have a strong influence on results that can be expected with a given

rate of herbicide. Since weather and growing conditions are so variable it is unlikely that results in one season or location can be precisely duplicated in the next.

SUMMARY AND CONCLUSIONS

1. Data on a 4-year study of chemical crabgrass control in Kentucky bluegrass turf are reported. The chemicals studied were sodium arsenite, phenyl mercuric acetate, potassium cyanate, monoamminoboronium fluoride (S–1840) and bis (lauryl, di2–hydroxyethylammino) boronium fluoride (S–1998).

2. Potassium cyanate, phenyl mercuric acetate, S–1840, and S–1998 provided crabgrass control averaging 89 per cent or more for the four years. Control with sodium arsenite averaged approximately 20 per cent less.

3. Turf injury ranked from least to greatest, was in the order phenyl mercuric acetate, potassium cyanate, S–1998, S–1840, and sodium arsenite as an average of the four years.

4. Phenyl mercuric acetate generally gave less temporary discoloration of the bluegrass turf but was more dependent on repeat treatments for crabgrass control than the other chemicals.

5. The boronium compounds appear to be equally as effective as potassium cyanate. As they are nonpoisonous and do not decompose on exposure, they offer an advantage over the potassium cyanate for commercial use.

6. Rates, in each application, of 8 to 16 pounds per acre of potassium cyanate and 20 to 30 pounds of the boronium compounds gave good crabgrass control comparable to that obtained with 0.7 to 0.9 pounds of phenyl mercuric acetate. Turf injury with these rates was not serious.

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The Influence of Various Carriers Upon the Inhibitory Effectiveness of 2,4–D Sprays[1]

MILTON E. GERTSCH[2]

INTRODUCTION

IT HAS been noted frequently that salts of 2,4–dichlorophenoxyacetic acid, such as sodium or triethanolamine salt, are effective as herbicides in regions of moderate rainfall, while in arid regions they are sometimes relatively ineffective. Usually, and particularly under arid conditions, the aliphatic esters of 2,4–D have been more effective as herbicides than the salt forms.

Ennis (3) found that kidney bean growth was inhibited to a greater degree when oil or a 5 per cent oil emulsion were used as carriers for isopropyl 2,4–D or 2,4,5–T than when water was used. Also, an application of triethanolamine 2,4–D in a wholly aqueous solution to soybeans inhibited growth less than similar 2,4–D applications in oil, 5 per cent oil emulsion, and in water with one per cent Tergitol 7. Ennis (4) concluded that the chief reason for the greater effectiveness of commercially prepared 2,4–D esters was probably the presence of the surface-active agents and oil in these formulations.

Gertsch and Ryker (6) reported that applications of tri-ethanolamine 2,4–D were more effective as herbicides for control of *Rosa bracteata* when a non-phytotoxic oil emulsion carrier was used than when water was used. In the course of these field studies it became desirable to evaluate more carefully water, water with surface-active agents, and oil emulsions as carriers for 2,4–D. Accordingly greenhouse experiments were conducted in which the depression of the top growth of the bean plant was used as the criterion for determining the relative herbicidal efficiency of 2,4–D applied in different carriers. The results of these tests are reported in this paper.

EXPERIMENTAL PROCEDURE

Black Valentine bush beans *(Phaseolus vulgaris)* were sprayed with the test materials and the amount of subsequent top growth was used as an index of the herbicidal efficiency. Except that the beans were grown in flats instead of pots, the method used was essentially the same as was outlined by Weaver (8). He applied various rates of 2,4–D to beans with expanded primary leaves and found an inverse relationship between the amount of 2,4–D applied and the amount of subsequent new growth which was produced. In the experiments reported here the extent of growth and the severity of treatment varied with the season. Thus in the different experiments the severity of reaction to a given treatment varied but the relationship of response between treatments did not differ materially. Some

[1]This work was done under an Esso Standard Oil Company fellowship in the Department of Botany, Bacteriology and Plant Pathology at Louisiana State University.

[2]Present address: E. I. DuPont deNemours & Co., Wilmington, Delaware.

experiments had to be discarded because either the plants died or stopped growing. To expedite making comparisons between experiments the treatment amine 2,4–D in water was used as a standard.

Greenhouse flats 9 inches by 18 inches were filled with sifted soil and were sterilized after which the beans were planted. When the primary leaves were nearly expanded and new shoot growth was just beginning, the plants were thinned to approximately 18 uniform plants per flat. A few hours prior to treatment the plants were well watered. When the shoot above the primary leaf node was 3 to 6 millimeters long, the flats were removed from the greenhouse for treatment and later returned to the greenhouse for the duration of the experiment. To simulate field applications of 2,4–D, the flats of beans were sprayed with 0.05 pound per acre acid equivalent of 2,4–D applied in 60 gallons of spray per acre by placing them on a 2 m.p.h. conveyor equipped with a No. 8006 Spraying System Nozzle operated at 18 p.s.i. suspended 18 inches above the bean foliage. There was continuous agitation of the spray material.

Nine to thirteen days after the plants had been treated, the first trifoliate leaf and all growth above the first trifoliate leaf node was harvested from 15 plants per flat and the fresh weight of this material was obtained. All experiments were of a randomized block design. The yields of the checks were considerably higher than those which had been treated with 2,4–D so they were not included in the analysis of variance. The least significant differences were calculated on the basis of the 5 per cent level.

In these experiments several non-phytotoxic oils† and a light naphtha (VM & P)† were used in the preparation of the emulsions used as the carriers for the 2,4–D.

The oils used and their initial and final boiling points were as follows:

	Initial B. P. °F.	*Final B. P.* °F.
Horticultural Spray Oil RDA–182 (referred to in text as 182)	410	600
VM & P Naphtha	249	297
RDA–123	350	410
Bayol J	615	751

Since the supplies of the last three oils listed were limited, and the responses of the bean plants did not seem to differ regardless of the oil used, the oil 182 was used in six of the seven experiments reported here. The surface-active agents used were Triton X–45†, Triton X–155†, Dreft, and Petroleum Sulfonate. In preparing the oil emulsions 1.0 volume per cent of the emulsifier was added to the oil and this mixture was added to the water. Thus, when 2, 10 or 20 per cent oil emulsion carriers were prepared the spray materials contained 0.02, 0.1 and 0.2 per cent, respectively, of the surface-active agent. In all the experiments, except where the effects of different concentrations of oil in the emulsion were evaluated, 10

†Supplied by the Esso Standard Oil Development Company, P. O. Box 51, Linden, New Jersey.

†Supplied by Rohm and Haas Co., Philadelphia 5, Pa.

per cent oil emulsions were used. This was done since 10 per cent oil emulsions had been used in the field work.

EXPERIMENTAL RESULTS

Evaluation of Oil Emulsions as 2,4–D Carriers

For an evaluation of oil emulsions as carriers for triethanolamine 2,4–D (amine 2,4–D), 10 per cent oil emulsions were prepared using the three oils, VM & P Naphtha, RDA–123 and Bayol J. In addition aqueous amine 2,4–D in water plus 0.1 per cent Triton X–45 was used. The results are given in Table 1.

Table 1. Yields from beans treated with 0.05 pound per acre of amine 2,4–D applied in various carriers. Triton X–45 (0.1%) was added to the aqueous 2,4–D spray and used to prepare the oil emulsions.

Carrier for amine 2,4-D	Average yield per flat
	gm.
Water	8.46
Water plus 0.1% Triton X-45	5.10
10% VM & P Naphtha Emulsion	4.83
10% RDA-123 Emulsion	5.36
10% Bayol J Emulsion	4.70
Untreated check	13.66

There was little difference in the inhibition which resulted from the use of the various oil emulsions or water plus 0.1 per cent Triton X–45 as the carriers for amine 2,4–D. When the 2,4–D was applied in water alone growth was not inhibited to the same extent as when 0.1 per cent Triton X–45 was included in the spray material.

To determine the influence of the concentration of oil in the emulsions, 2 and 20 per cent oil 182 emulsions, water alone, and water with 0.2 per cent Triton X–45 were used as carriers for triethanolamine 2,4–D or polypropylene glycol butyl ether ester 2,4–D.† The results are shown in Table 2.

Table 2. Yields from beans treated with 0.05 pound per acre of amine salt or polypropylene glycol butyl ether ester 2,4–D in various carriers.

Form of 2,4-D and Carrier	Average yield per flat*
	gm.
Amine in water	4.53
Amine in 2% 182 emul. (0.02% Triton X-45)	3.60
Amine in 20% 182 emul. (0.2% Triton X-45)	1.70
Amine in water with 0.2% Triton X-45	1.50
Ester in water	4.30
Ester in 2% 182 emul. (0.02% Triton X-45)	3.13
Ester in 20% 182 emul. (0.2% Triton X-45)	1.43
Untreated check	6.20

*Difference significant at .01 level: L.S.D. 1.17 gm.

†H–1010 supplied by Dow Chemical Co., Midland, Mich.

The higher the concentration of the oil in the emulsion, the greater was the amount of inhibition. When the amine 2,4–D spray material contained 0.2% Triton X–45, whether oil 182 was present or not, the inhibition of bean growth was similar. When oil 182 emulsions were used as carriers for the amine or ester 2,4–D, there tended to be more inhibition of bean growth than when water was used as the carrier for these two forms of 2,4–D.

For further evaluation of the effects of water and a 10 per cent 182 emulsion, (made with 0.1 per cent Triton X–45), as carriers for amine 2,4–D, two successive treatments of these carriers, both with and without 2,4–D, were applied. Thus the application of the 2,4–D may have been preceded or followed by an application of only a carrier. The second treatments were applied either fifteen minutes or two and one-half hours after the first treatment. The results of this experiment are shown in Table 3.

Table 3. Yields from beans treated with two successive applications. The interval of time between treatments was 15 minutes or 2½ hours. Amine 2,4–D was applied at the rate of 0.05 pound per acre.

First treatment	Second treatment	Average yield per flat*	
		15 min. between treatments	2½ hours between treatments
		gm.	gm.
2,4-D in water	None	3.77	
10% 182 emulsion	2,4-D in water	3.90	6.10
10% 182 emulsion	2,4–D in 10% 182 emulsion	2.73	4.20
2,4-D in water	10% 182 emulsion	3.43	1.73
2,4-D in water	Water, 60 gal./acre	5.87	3.03
2,4-D in 10% 182 emulsion	None	2.73	
Untreated check		10.4	

*Differences significant at .01 level: L.S.D. 1.89 gm.

Bean growth was inhibited more when the time interval between the application of a 10 per cent oil 182 emulsion alone and the subsequent application of amine 2,4–D in water was 15 minutes than when it was 2½ hours. Equal inhibition of bean growth resulted from applications of a 10 per cent oil 182 emulsion followed 15 minutes later by amine 2,4–D in a 10 per cent oil 182 emulsion and from a single treatment of amine 2,4–D in a 10 per cent oil 182 emulsion. However, while the differences in yield are slightly less than required for significance, applications of the former treatments resulted in less inhibition when the period between treatments was two and one-half hours. Bean growth was inhibited most by an application of amine 2,4–D in water followed by an application of a 10 per cent oil 182 emulsion two and one-half hours later. The growth of the beans was more inhibited by an application of amine 2,4–D in water than by an identical herbicidal application followed 15 minutes later by an application of 60 gallons of water per acre.

To determine the influence of various carriers on the effectiveness of different forms of 2,4–D, water alone, water plus 0.1 per cent

Triton X–155, and a 10 per cent oil 182 emulsion prepared with 0.1 per cent Triton X–155 were used as carriers for three water soluble forms of 2,4–D, triethanolamine salt, sodium salt, and polyethylene glycol ester.† The results from this experiment are shown in Table 4.

Table 4. Yields from beans treated with 0.05 pound per acre of sodium salt, polyethylene glycol ester or triethanolamine salt of 2,4–D in three carriers.

Carrier for 2,4-D	Average yield per flat[a]			
	Amine 2,4-D	Ester 2,4-D	Na 2,4-D	Average[c]
	gm.	gm.	gm.	gm.
Water	7.67	8.36	10.26	8.77
Water plus 0.1% Triton X-155	2.83	4.90	11.23	6.32
10% 182 emulsion (X-155)	1.70	1.53	9.50	4.24
Average[b]	4.07	4.93	10.33	—
Untreated check	13.76			

[a]Interaction differences significant at .01 level: L.S.D. 2.45 gm.
[b]Differences significant at .01 level: L.S.D. 1.42 gm.
[c]Differences significant at .01 level: L.S.D. 1.42 gm.

Applications of amine 2,4–D or polyethylene glycol ester 2,4–D inhibited the growth of beans more than Na 2,4–D and the yields did not differ appreciably when Na 2,4–D was applied in the various carriers. Least inhibition resulted from applications of the amine or ester 2,4–D when water was used as the carrier, intermediate inhibition when 0.1 per cent Triton was added to the aqueous spray material, and most inhibition when the 10 per cent oil 182 emulsion was used as the carrier. Yields were similar when the ester and amine forms of 2,4–D were used with the same kind of carrier.

Determining the Effects of Surface-Active Agents

To determine the influence of surface-active agents in the carriers on the effectiveness of 2,4–D, water alone, water with 0.05 per cent Dreft (0.5 gm. per liter), water with 0.1 volume per cent Triton X–45, and a 10 per cent oil 182 emulsion prepared with 0.1 per cent Triton X–45, were used as carriers for polypropylene glycol butyl ether ester and amine 2,4–D. The results are shown in Table 5.

Amine 2,4–D applied in water inhibited bean growth less than comparable applications with water and surface-active agents or a 10 per cent oil 182 emulsion, but the effectiveness of the ester 2,4–D was increased only by the 10 per cent oil 182 emulsion carrier. When the ester form of 2,4–D was used the yields were similar when water alone or water with the surface-active agents were used as carriers, but considerably more inhibition resulted when a 10 per cent oil 182 emulsion was used as the carrier. When the oil emulsion was used as the carrier for the 2,4–D ester, the bean plants were dead or dying at the end of the experiment.

Table 6 shows the yield data obtained and materials which were

†ACP–648, supplied by the American Chemical Paint Co., Ambler, Pa.

Table 5. Yields from beans treated with 0.05 pound per acre of amine salt or polypropylene glycol butyl ether eseter 2,4–D in various carriers.

Carrier for 2,4-D	Average yield per flat		
	Form of 2,4-D[a]		Average for carriers[b]
	Amine	Ester	
	gm.	gm.	gm.
Water	13.43	1.36	7.40
Water plus 0.05% Dreft	4.06	1.36	2.72
Water plus 0.1% Triton X-45	3.86	1.93	2.90
10% 182 emulsion (0.1% Triton X-45)	4.00	0.20	2.10
Average for forms of 2,4-D[c]	6.34	1.21	
Untreated check	23.20		
10% 182 emulsion check	20.76		

[a]Interactions differences significant at .01 level: L.S.D. 0.8 gm.
[b]Differences significant at .01 level: L.S.D. 0.8 gm.
[c]Differences significant at .01 level: L.S.D. 0.4 gm.

Table 6. Yields from beans treated with 0.05 pound per acre of aqueous amine 2,4–D with various surface active agents added.

Carrier for Amine 2,4-D	Average yield per flat*
	gm.
Water plus 0.05% Dreft	9.23
Water plus 0.1% Triton X-45	9.16
Water plus 0.1% Triton X-155	4.83
Water plus 0.1% Petroleum Sulfonate	8.26
Untreated check	18.27
Water plus 0.1% Triton X-45 check	18.83

*Differences significant at 0.05 level. L.S.D. 0.59 gm.

used to compare further the effect of various surface-active agents.

The yields were significantly lower when Triton X–155 was used as the surface-active agent than when the other surface-active materials were added to the amine 2,4–D spray material.

For evaluating the influence of the concentration of the surface-active agents in the spray material, three concentrations of the surface-active agents, Triton X–45 and Triton X–155 in water, and oil emulsions prepared by using these same materials were used as carriers for amine 2,4–D. To prevent excessive wilting of plants in an unshaded greenhouse during this experiment, it was necessary to spray the greenhouse and plants lightly with water twice on the day the 2,4–D sprays were applied. While this was not done until several hours after the herbicidal application, the amount that may have been washed off is not known.

The concentrations of the surface-active agents used and the yields obtained are shown in Table 7. In this experiment the least significant difference was abnormally high.

While the differences in yield were below significance, there was consistently more inhibition from the use of Triton X–155 and the higher the concentration of the surface-active agent in the 2,4–D carrier, the lower the yield obtained. The amine 2,4–D when applied in a 10 per cent oil 182 emulsion was the most effective for inhibiting

Table 7. Yields from beans treated with 0.05 pound per acre amine 2,4–D in various carriers prepared with different amounts of two surface-active agents.

Treatment	Average yield per flat		
	Triton X-45	Triton X-155	Average*
	gm.	gm.	gm.
Amine 2,4-D in water	8.67	—	8.67
Amine 2,4-D in water plus 0.001% Triton	7.70	5.83	6.77
Amine 2,4-D in water plus 0.01% Triton	7.27	5.23	6.25
Amine 2,4-D in water plus 0.1% Triton	5.60	4.57	5.08
Amine 2,4-D in 10% 182 emulsion (0.1% Triton)	Nil	Nil	Nil
10% 182 emulsion check	18.50	20.67	
0.1% Triton check	18.00	—	
Untreated check	19.67		

*Differences significant at 0.05 level: L.S.D. 3.48 gm.

the growth of the beans. The higher the quantity of the surface-active agent in the spray material, the more the spray droplets spread on the foliage. Spray droplets of the 10 per cent 182 oil emulsion coalesced and spread over the surface of the leaf.

DISCUSSION

Several experiments were carried out in an attempt to arrive at some explanation for the different degrees of inhibition of bean growth which resulted from applications of 2,4–D in water, oil emulsions, or water with surface-active agents. The yield data indicate a low order of toxic effect by the oils used in the emulsions. Therefore, factors other than toxicity of the oil were probably responsible for the increased effectiveness of the 2,4-D sprays.

The data of the experiments revealed that several oil emulsions were equally effective as carriers for amine 2,4–D and also that water with the surface-active agents was frequently as effective as carriers for amine 2,4–D. When 2 per cent and 20 per cent oil 182 emulsions, water alone, and water with the surface-active agent Triton X–45 were compared as carriers for amine 2,4–D, water was found to be least effective, the 2 per cent emulsion somewhat more effective, and water with 0.2 per cent Triton X–45 or 20 per cent oil 182 emulsion (made with 0.2 per cent Triton X–45), the most effective for inhibiting growth. When these oil 182 emulsions were used as carriers for polypropylene glycol butyl ether ester 2,4–D, the inhibition was greater the higher the oil content of the emulsion.

The yields as shown in Table 3 indicate that a light application of water after the original spray material had dried did not increase the severity of injury caused by an aqueous amine 2,4–D application. Hence, it seems unlikely that the effect of the oil emulsion carriers was one of retaining a water vehicle for a longer period of time. These data also show that when an application of a 10 per cent oil 182 emulsion was followed shortly by an application of amine 2,4–D in water or in an oil emulsion, the results did not differ appreciably from those cases in which only the latter treatment was applied. However, when the interval of time between

treatments was 2½ hours, the inhibition was somewhat less, thus indicating a protective action by the oil emulsion. It is of interest to note that the yields from plants which received an application of aqueous amine 2,4–D which in 15 minutes was followed by an application of a 10 per cent oil 182 emulsion were similar to those from plants which had received only an application of amine 2,4–D in a 10 per cent oil 182 emulsion.

It is indicated that the surface-active agents were chiefly responsible for increasing the effectiveness of amine 2,4–D. However, the data also show that the oil, not the detergent, was the agent increasing the effectiveness of the oil soluble polypropylene glycol butyl ether ester 2,4–D. This is of interest because several workers (1, 2, 5, 7) have reported increases in the effectiveness of aqueous 2,4–dichlorophenoxyacetic acid when various adjuvants were used.

The lack of response of the polypropylene glycol butyl ether ester 2,4–D sprays to the addition of detergents may have been due to an ample supply of a surface-active agent in the commercial preparation. Since the ester was oil soluble, it probably existed in the oil phase of the oil 182 emulsions. This oil apparently penetrated the bean foliage without difficulty, since no oil could be detected on the surface of the foliage a few hours after treatment. It therefore seems plausible that the penetration of the 2,4–D ester may have been facilitated by the presence of the oil in the carrier which readily penetrated the cuticle.

When several surface-active agents were compared as to their capacity to increase the effectiveness of aqueous amine 2,4–D spray solutions, Triton X–155 was found to be the best of those tested. Tables 6 and 7 show that up to 0.1 per cent the quantity and kind of surface-active agent employed are important factors in increasing the effectiveness of amine 2,4–D. There was no indication that the surface-active agents *per se* were toxic to the beans.

The addition of a surface-active agent to aqueous sprays or the use of 10 per cent oil 182 emulsion carriers did not increase the effectiveness of Na 2,4–D. However, the water soluble polyethylene glycol ester 2,4–D applied in the various carriers produced results similar to those from amine 2,4–D. The spreading action of the spray material on the bean foliage seemed to be a direct function of the quantity of the detergent, i.e., with 0.001 per cent Triton X–45 or X–155 there was a slight spreading action, whereas there was considerable spreading when 0.1 per cent of these detergents was used. When the carrier was a 10 per cent oil 182 emulsion the droplets of spray readily coalesced and spread over the surface of the leaf, with a tendency to accumulate on the veins. Also, when oil emulsion carriers were used, the foliage maintained a moist appearance for a longer period of time.

While there may be several factors in the increased effectiveness of amine 2,4–D or the water soluble polyethylene glycol ester 2,4–D applied in water with surface-active agents or in oil emulsions, it seems most logical, however, that the surface-active agents served as a penetrant, i.e., they served to facilitate the entrance of more

2,4–D into the plant. The preparations of both amine 2,4–D and polyethylene glycol ester 2,4–D were found to be soluble in Triton X–45 or X–155 whereas Na 2,4–D was not. It would seem that if the spreading of the spray material were the chief operative factor, then the effectiveness of Na 2,4–D would have been increased by the addition of Triton X–155.

It is conceivable that when applications of aqueous amine 2,4–D or polyethylene glycol ester 2,4–D were made with one of the Tritons, the Triton softened the cuticle, partially removed the cuticle, or rendered the cuticle more permeable to the 2,4–D. The experimental results obtained seem to indicate that when the water evaporated from the foliage, which usually required only a few minutes, the 2,4–D became concentrated in the small amount of Triton which also existed outside the leaf. Part of the Triton molecules are relatively soluble in aromatic and aliphatic hydrocarbons and they probably penetrated into the cuticle. Since the Triton surface-active agents used readily hydrate, numerous water molecules were presumably also associated with the Triton on the leaf surface. Therefore, the 2,4–D probably became concentrated in the surface-active agent which served as a cosolvent to facilitate the entry of the 2,4–D into the plant.

SUMMARY

In these experiments the inhibition of the new growth of Black Valentine bush beans was used as the index of the effectiveness of 0.05 pound per acre of 2,4–D applied in various carriers. The amount of new growth was determined by weighing the fresh plant material produced in nine to thirteen days after treatment.

When comparisons were made of the effects of water, oil emulsions prepared with surface-active agents, and water with surface-active agents as carriers for triethanolamine 2,4–D, least inhibition resulted from the use of water alone, and most inhibition when oil emulsions were used. There was slightly less inhibition when water with the surface-active agent was employed than when oil emulsions prepared with the same quantity of surface-active agent were used as the carrier for amine 2,4–D.

Applications of triethanolamine 2,4–D in various carriers were preceded or followed by an application of the carriers alone. The results indicated that the greater effectiveness of triethanolamine 2,4–D applied in a 10 per cent oil 182 emulsion was not due to the prolonged presence of an aqueous carrier on the foliage, but rather, was due to other materials in the emulsion.

There was consistently more inhibition when the surface-active agent Triton X–155 was added to the triethanolamine 2,4–D spray material than when Triton X–45 was added. The highest concentration of the surface-active agent used was 0.1 volume per cent and while the differences in yield were small, inhibition was proportional to the concentration of the adjuvant in the spray material.

When the water soluble polyethylene glycol ester 2,4–D or triethanolamine 2,4–D were applied in three different carriers, the

inhibition was least when water was used, highest when a 10 per cent oil (182) emulsion was used, and intermediate when water and 0.1 per cent Triton X–155 were employed. There were little differences in the yields of beans treated with sodium 2,4–dichlorophenoxy acetate in these various carriers.

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The Relation of Structural Configuration to the Herbicidal Properties and Phytotoxicity of Several Carbamates and Other Chemicals

W. S. Shaw and C. R. Swanson[1]

The discovery of the herbicidal properties of isopropyl N-phenylcarbamate (IPC) and isopropyl N-(3-chlorophenyl)carbamate (CIPC) and other organic chemicals has created an impetus in the development of new herbicides. Since the discovery of 2,4-dichlorophenoxyacetic acid (2,4-D), considerable effort has been devoted to the development of herbicides that are as effective and selective for the control of annual grasses as is 2,4-D for the control of many broadleaved weeds.

The study reported herein is an attempt to expand our knowledge of the herbicidal properties of the carbamates and to investigate the relationships among structural configuration, mode of action, specificity and herbicidal activity.

Review of Literature

The biological activity of compounds of the urethane series upon animals has been demonstrated (8) since 1927. However, in 1929 it was reported (11) that phenylurethane retarded the germination of oats and wheat and resulted in abnormal growth of the seedlings. Since 1929 several workers (12, 13, 16, 17) have conducted research on the effects of various urethanes upon plants.

The discovery of isopropyl N-phenylcarbamate (18) was especially interesting since this chemical as well as other aryl carbamic esters was shown to exhibit selective herbicidal action on monocotyledonous plants with little or no injury to dicotyledonous plants. This action appeared to be the converse of the action observed in the phenoxyacetic acid class of compounds. The discovery stimulated further research and many investigators began to evaluate the herbicidal properties of IPC.

Early attempts to control grasses with IPC were disappointing, but further research (7) showed that the chemical was a mitotic poison capable of producing striking cytological aberrations in some species. Other workers (5, 6, 10) showed that IPC was most effective when applied to the soil and absorbed through the roots of plants. These same investigators also studied the effects of the chemical on a large number of plants and concluded that IPC was much more effective against monocotyledonous plants than dicotyledonous plants. It was also demonstrated that grasses vary greatly in their degree of tolerance or susceptibility to IPC (14). Greatest inhibition of growth was always observed when the compound was applied to

[1]Agronomist and Associate Plant Physiologist respectively, Division of Weed Investigations, Bureau of Plant Industry, Soils and Agricultural Engineering, U. S. Department of Agriculture, Beltsville, Maryland. The chemicals used in this study, except as indicated, were supplied by U. S. Industrial Chemicals Co., Division of National Distillers Products Corporation, Baltimore, Maryland.

the soil prior to emergence of the grasses or to very young seedlings. One of the greatest limitations in the use of IPC as a herbicide has been its failure to control crabgrass *(Digitaria spp.)* and other weedy grasses (14). This high degree of specificity and selectivity in action has at the same time made it highly valuable for the control of annual ryegrass in legume seed fields (10).

The discovery of the herbicidal properties and especially the effectiveness of isopropyl N-(3-chlorophenyl)carbamate (3,7) for the selective control of crabgrass and other grasses tolerant to IPC has led to intensive investigations of this chemical for selective weed control in cotton, soybeans, alfalfa, and many other dicotyledonous crop plants.

Early work with the carbamates (18) and later work with various alkyl esters of N-phenylcarbamic acid (9) followed by the voluminous literature that has developed recently on the use of isopropl N-(3-chlorophenyl)carbamate for weed control in several dicotyledonous crops suggests the need for a through evaluation of the herbicidal properties of the family of carbamates and related compounds.

MATERIALS AND METHODS

A macro screening technique as previously described (15) was used to evaluate the herbicidal and phytotoxic properties of the chemicals under greenhouse conditions. The experimental design used was a randomized plot with 3 replications. Corn *(Zea mays)* hybrid US13, wheat *(Triticum vulgare)* variety Thorne, cotton *(Gossypium hirsutum)* variety Delta Pine 15, and soybean *(Soja max)* variety Hawkeye were used as test crop plants. Test plants considered as weeds were crabgrass *(Digitaria sanguinalis)*, annual ryegrass *(Lolium multiflorum)*, rough pigweed *(Amaranthus retroflexus)* and mustard *(Brassica kaber)*.

Metal flats, 14″x20″, stamped from galvanized sheet metal, were used as containers in which the plants were grown. The crop plants were seeded in single rows per flat as follows: corn 15 seeds, wheat 40 seeds, cotton 30 seeds and soybeans 15 seeds. Each crop was seeded at a depth of 1¼ inches. The weeds were seeded on a volume basis per flat at a depth of ¼ inch as follows: mustard 3 cc., pigweed 1 cc., ryegrass 4 cc., and crabgrass 3 cc.

Each chemical, except as indicated in Table 1, was applied as a pre-emergence spray at rates of 2, 8 and 16 pounds per acre immediately after planting.

Each rate of each chemical was dissolved or suspended in a spray mixture of 5 percent acetone, 2 percent wetting agent[2] and 93 percent water and applied at the volume of 40 gallons of spray mixture per acre. The chemicals were applied using an experimental application table (15) with an endless conveyor belt which transported the seeded flats under the spray nozzles. The table was calibrated to deliver 40 gallons of spray mixture per acre when operated at 2 m.p.h. and a pressure of 30 p.s.i. was maintained.

[2]Tween 20, a nonionic wetting agent, was supplied by the Atlas Powder Company.

The "soil" was a composted greenhouse potting soil consisting of two-thirds loam and one-third sand. After applying the chemicals, the sprayed flats were transferred to subirrigation tanks and subirrigated to field capacity. An adequate moisture content was maintained throughout the experiments by subirrigation techniques (15) and no water was added to the surface of the flats after the chemicals were applied. The greenhouse day temperatures were maintained at 85° to 90°F while night temperatures ranged from 65° to 70°F.

The data in Table 1 were obtained by making an injury rating on all plants, determining the height reduction of the crop plants, and determining the percentage of plants killed. The injury rating scale was as follows: 0, no visible effect; 1,2,3, slight injury, plants usually recover with little or no reduction in top growth; 4,5,6, moderate injury, plants usually recover but with reduced top growth; 7,8,9, severe injury, plants usually do not recover; 10, all plants killed. The height of all crop plants was measured and expressed as a percentage height reduction when compared with an untreated check as follows: $(\frac{C\text{-}T}{C} \times 100) = \%$ height reduction. The percent crop plants killed was determined by counting the number of plants emerged and expressing the result as the percentage killed when compared to an untreated check as follows: $(\frac{C\text{-}T}{C} \times 100) = \%$ kill. The percentage weed kill was determined by two independent visual estimates. Thus the results in Table 1 are based on two quantitative determinations and one estimate.

All chemicals in Table 2 with a phytotoxicity rating of very active were retested in the greenhouse and the results obtained agreed with those reported in Table 2.

In field studies, 29 of the most active carbamates in Table 2 were evaluated as pre-emergence herbicides at 8 and 16 pounds per acre and as post-emergence treatments at 3 and 6 pounds per acre on 30 plant species.

Preliminary studies have been conducted on the persistence of herbicidal activity of 20 of the most active carbamates in the soil under greenhouse conditions. Each chemical at 2, 8 and 16 pounds per acre was applied to the surface of the soil in greenhouse flats and immediately mixed in the upper 1½ inches of soil. The same crops and weeds were seeded at the depths and in the manner previously described at monthly intervals after treatment. After each 30 day period for 3 successive replantings the crop and weed response to the residual toxic effects of the chemicals in the soil was measured in the same manner as described previously.

EXPERIMENTAL RESULTS AND DISCUSSION

The responses of eight plant species to several carbamates and other chemicals of known herbicidal properties are indicated in Tables 1 and 2.

Table 1—The response of eight plant species to several carbamate derivatives and other chemicals applied as pre-emergence sprays.

Chemical name	Rate per A lbs.	Crops												Weeds							
		Cotton			Soybeans			Corn			Wheat			Mustard		Pigweed		Ryegrass		Crabgrass	
		Inj. rat. No.	Ht. red. Pct.	Plt. k. Pct.	Inj. rat. No.	Ht. red. Pct.	Plt. k. Pct.	Inj. rat. No.	Ht. red. Pct.	Plt. k. Pct.	Inj. rat. No.	Ht. red. Pct.	Plt. k. Pct.	Inj. rat. No.	Plt. k. Pct.	Inj. rat. No.	Plt. k Pct.	Inj. rat. No.	Plt. k. Pct.	Inj. rat. No.	Plt. k. Pct.
Ethyl N-phenyl carbamate	2	2	0	14	2	0	6	2	0	11	2	6	10	4	47	2	17	7	70	2	10
	8	1	2	0	1	0	0	3	0	18	3	3	7	0	0	0	0	8	80	0	0
	16	0	0	22	1	14	19	1	5	3	2	2	27	3	17	3	20	7	20	2	17
2-Chloroethyl N-(3-chlorophenyl) carbamate	2	2	5	0	2	8	9	4	10	25	4	19	3	2	30	2	10	5	37	4	13
	8	1	0	0	1	0	0	5	0	15	2	0	20	9	90	9	95	9	93	9	88
	16	1	3	20	2	0	4	0	0	0	2	2	17	7	77	8	85	9	73	9	73
Propyl N-phenyl carbamate	2	0	5	0	0	0	0	0	4	11	0	8	0	0	3	0	3	0	3	0	0
	8	1	0	31	1	19	0	0	0	5	1	0	25	1	7	1	7	6	65	0	3
	16	1	8	0	2	27	7	1	10	0	2	6	2	7	91	7	90	10	100	10	100
3-Chloropropyl N-phenyl carbamate	2	0	0	7	0	0	0	1	0	0	1	0	13	1	10	1	7	0	0	0	0
	8	0	0	10	0	2	0	0	0	0	0	0	3	3	32	3	27	0	0	2	14
	16	0	0	0	0	0	0	0	0	0	0	0	0	7	82	6	7	8	55	7	57
Isopropyl N-phenyl carbamate[1]	2	0	0	3	0	4	0	0	3	0	1	0	8	0	0	0	0	7	73	1	0
	8	0	19	28	0	7	23	0	15	11	1	2	7	4	30	3	23	9	97	1	10
	16	0	0	6	2	9	15	1	3	0	1	0	17	5	53	2	33	9	98	3	17
Isopropyl N-(2-chlorophenyl) carbamate	2	0	5	0	1	0	12	1	4	11	1	19	0	0	0	0	0	1	10	0	3
	8	1	0	0	1	0	9	2	0	11	3	19	21	1	7	0	0	7	82	0	0
	16	9	67	81	9	56	67	7	40	5	6	55	37	1	0	9	93	10	100	9	98
Isopropyl N-(3-chlorophenyl) carbamate[2]	2	1	0	0	1	2	10	2	4	8	2	4	20	8	53	7	47	9	87	7	53
	8	2	0	20	4	11	17	4	7	5	4	9	27	9	57	9	70	9	95	9	63
	16	0	0	6	2	2	2	3	3	0	6	2	53	9	90	9	95	9	98	9	93
Isopropyl N-(3-chlorophenyl carbamate[3]	2	1	0	6	2	25	0	2	4	21	1	0	30	9	90	6	42	9	93	9	47
	8	0	0	12	4	32	0	2	3	2	4	2	22	9	87	9	85	9	95	9	98
	16	3	23	23	7	44	0	3	23	0	6	6	38	9	97	9	97	9	98	10	100
Isopropyl N-(3-chlorophenyl)-carbamate[4]	2	2	10	0	2	0	0	6	0	11	2	14	20	9	75	9	80	9	92	9	63
	8	1	26	0	2	2	0	5	0	5	2	10	14	9	88	9	95	9	98	9	87
	16	3	25	5	6	60	2	7	34	0	8	29	10	10	100	10	100	10	100	10	100
Isopropyl N-(4-chlorophenyl) carbamate[5]	2	0	6	6	0	0	13	0	8	0	2	4	8	0	0	0	0	2	13	0	0
	8	2	0	17	2	7	4	0	5	0	2	0	7	3	27	3	33	7	57	1	7
	16	2	12	22	3	20	2	1	8	0	2	6	12	6	63	8	37	8	57	4	40

Isopropyl N-(4-chlorophenyl) carbamate[6]	2	0	0	0	7	0	0	7	0	7	2	3	0	0	0	1	7	4	28	6	3	
	8	2	0	0	3	4	9	3	10	13	3	18	17	6	60	6	43	7	40	4	27	
	16	3	25	11	4	27	5	1	9	0	2	18	0	1	6	5	70	7	37	2	10	
Isopropyl N-(2,4-dichlorophenyl) carbamate	2	0	0	0	0	0	0	0	1	7	0	16	0	0	0	0	0	0	0	0	0	
	8	0	0	0	0	0	0	0	0	9	0	9	0	0	0	0	0	1	0	1	0	
	16	9	79	96	8	75	62	5	34	23	5	31	30	4	10	9	95	8	83	2	20	
Isopropyl N-(3,6-dichlorophenyl) carbamate	2	0	0	0	0	0	0	2	3	7	1	21	7	1	3	1	3	5	40	0	0	
	8	2	2	0	2	0	0	2	0	13	2	8	20	1	10	2	23	6	77	3	30	
	16	9	71	85	9	73	69	7	36	10	7	46	43	9	83	9	98	9	99	9	99	
Isopropyl N-(3,4-dichlorophenyl) carbamate	2	0	5	0	0	0	0	1	0	11	2	18	3	0	0	2	20	1	7	0	0	
	8	0	0	0	0	0	0	1	0	5	1	3	3	1	3	4	53	4	30	2	10	
	16	9	0	92	9	98	98	5	38	12	4	29	30	2	7	10	100	5	33	0	0	
Isopropyl N-(3,5-dichlorophenyl) carbamate	2	0	0	0	0	0	0	0	0	7	0	13	0	0	0	0	0	1	7	0	0	
	8	0	0	0	0	0	0	0	0	0	0	3	0	0	0	0	0	0	0	0	0	
	16	9	79	99	7	52	47	4	28	10	5	31	33	2	3	9	93	3	30	0	0	
Isopropyl N-(3-nitrophenyl) carbamate	2	1	0	0	1	0	0	1	0	5	0	5	7	1	13	1	20	1	3	0	0	
	8	1	24	24	1	0	25	1	0	5	1	0	3	2	20	8	85	4	50	9	67	
Isopropyl N-(4-nitrophenyl) carbamate	2	0	0	0	0	4	0	1	0	2	2	7	17	0	0	0	0	2	23	1	7	
	8	0	0	0	0	0	0	3	1	20	4	22	7	0	0	0	0	4	37	1	3	
Isopropyl N-(2-methylphenyl) carbamate	2	1	0	29	1	6	2	1	1	13	1	0	17	1	0	0	0	0	0	0	0	
	8	0	0	0	0	0	0	0	0	0	0	1	0	0	0	0	0	4	47	0	0	
	16	0	0	1	0	0	0	0	0	0	0	0	0	0	0	1	10	8	85	0	0	
Isopropyl N-(3-methylphenyl) carbamate	2	1	0	0	1	0	0	2	0	7	3	10	12	4	30	2	10	9	97	2	20	
	8	2	0	0	2	0	0	7	17	15	3	19	13	9	87	9	90	10	100	9	77	
	16	2	9	29	2	2	2	2	4	13	2	0	20	9	93	9	95	9	98	9	93	
Isopropyl N-(4-methylphenyl) carbamate	2	0	0	17	0	0	2	0	0	0	0	0	0	0	0	0	0	2	7	1	0	
	8	0	0	12	1	0	0	0	0	0	1	0	0	0	3	0	0	3	2	0	3	
	16	0	2	10	1	1	0	0	0	0	2	0	20	1	10	2	17	4	13	4	48	
Isopropyl N-(3-acetophenyl) carbamate	2	1	0	0	1	0	4	1	0	9	1	1	8	0	0	0	0	5	60	0	0	
	8	1	7	0	1	0	0	0	0	5	2	0	12	0	0	4	53	9	93	3	43	
	16	0	12	24	0	0	0	0	3	3	1	7	7	0	0	0	0	0	0	1	7	
Isopropyl N-(4-acetophenyl) carbamate	2	0	0	0	0	0	0	0	0	2	0	6	0	0	0	0	0	1	3	0	0	
	8	1	0	0	0	0	6	0	0	11	0	2	0	0	0	0	0	1	7	1	7	
	16	2	13	17	2	13	5	1	9	0	0	6	0	0	0	4	37	1	17	0	0	
Isopropyl N-(2-methoxyphenyl) carbamate	2	1	0	0	0	0	9	0	0	2	1	4	0	1	13	0	0	2	10	0	0	
	8	2	0	0	2	6	0	1	0	5	2	9	10	6	53	3	27	8	80	2	13	
	16	2	25	0	5	48	9	3	5	0	2	9	9	9	88	9	99	10	100	10	100	

Table 1—(Continued)

Chemical name	Rate per A lbs.	Crops												Weeds							
		Cotton			Soybeans			Corn			Wheat			Mustard		Pigweed		Ryegrass		Crabgrass	
		Inj. rat. No.	Ht. red. Pct.	Plt. k. Pct.	Inj. rat. No.	Ht. red. Pct.	Plt. k. Pct.	Inj. rat. No.	Ht. red. Pct.	Plt. k. Pct.	Inj. rat. No.	Ht. red. Pct.	Plt. k. Pct.	Inj. rat. No.	Plt. k. Pct.	Inj. rat. No.	Plt. k Pct.	Inj. rat. No.	Plt. k. Pct.	Inj. rat. No.	Plt. k. Pct.
Isopropyl N-(3-chloro,6-methoxyphenyl) carbamate	2	1	0	0	1	0	0	3	7	9	3	20	0	0	0	0	0	2	17	1	3
	8	3	2	33	1	0	0	1	0	7	2	13	23	6	73	9	97	5	67	9	83
	16	9	83	94	7	56	33	3	28	0	4	28	13	9	98	10	100	9	98	9	95
Isopropyl N-(3-trifluoromethylphenyl) carbamate	2	0	0	0	0	0	0	0	0	0	0	0	0	1	10	1	10	2	17	2	7
	8	1	0	7	0	0	0	0	0	0	0	0	3	3	33	3	35	2	17	1	7
	16	0	0	0	1	0	8	0	0	0	0	0	3	4	38	4	33	8	80	6	5
Isopropyl N-(4-dimethylaminophenyl) carbamate	16	2	17	12	3	21	9	0	9	0	0	10	0	0	3	2	27	0	0	0	0
Isopropyl N-(4-dimethylaminophenyl) carbamate methiodide	2	0	0	0	0	0	18	0	12	5	0	0	0	0	0	0	0	0	0	0	0
	8	0	24	0	0	0	0	0	4	13	0	13	0	0	0	0	0	0	0	0	0
	16	3	25	15	2	10	7	0	7	0	0	13	0	0	0	1	13	0	0	0	0
Isopropyl N-(3-hydroxyphenyl) carbamate	2	0	0	0	0	0	0	0	0	9	0	7	0	0	0	0	0	0	0	0	0
	8	1	2	0	1	0	0	1	7	11	1	6	5	0	0	0	0	1	3	1	3
	16	0	0	10	0	0	2	0	8	0	0	0	0	0	0	0	0	0	0	0	0
Isopropyl N-(2-furfuryl) carbamate	2	0	0	0	0	0	0	0	0	13	0	4	0	0	0	0	0	1	3	0	0
	8	1	0	0	1	0	15	2	4	9	2	12	7	0	0	0	0	1	0	0	0
	16	2	17	20	4	25	18	1	5	0	2	13	12	2	23	7	80	1	3	0	0
Isopropyl N-(2-pyridyl) carbamate	2	0	15	31	0	0	2	0	3	0	0	1	0	0	0	0	0	0	0	0	0
	8	0	0	0	0	0	0	0	0	0	0	1	0	0	0	0	0	0	0	0	0
	16	9	88	99	8	67	69	3	26	0	4	25	0	4	47	10	100	5	17	0	0
Isopropyl N-phenylthiono carbamate	2	0	0	0	0	0	0	2	3	9	2	23	0	0	0	0	0	5	33	0	0
	8	1	0	0	3	0	0	6	0	13	3	1	20	6	60	7	57	9	98	7	53
	16	4	29	21	6	63	11	5	36	0	2	19	7	9	99	10	100	10	100	10	100
Isopropyl N-(4-phenylazophenyl) carbamate	2	0	0	0	0	0	0	0	0	13	0	22	0	0	0	0	0	0	0	0	0
	8	1	5	0	0	0	0	3	0	15	2	10	0	0	1	0	3	2	7	2	7
	16	0	8	0	1	8	5	0	2	0	1	6	0	2	12	2	17	0	0	0	0
n-Butyl N-phenyl carbamate	2	0	0	0	1	0	0	3	10	18	2	13	3	0	0	0	0	0	2	1	3
	8	1	5	0	2	0	6	3	7	18	3	14	12	6	68	2	21	5	60	2	13
	16	9	71	91	9	94	91	4	33	3	5	46	17	9	91	10	100	8	6	0	0

Isopropyl N-(3-chloro-6-methylphenyl)carbamate[12]	2	2	13	7	0	9	5	0	3	0	0	13	0	1	3	4	37	8	85	8	57
	8	2	13	2	3	28	0	5	47	0	3	11	0	2	3	7	63	9	95	9	93
	16	0	14	0	1	17	8	6	52	0	1	7	0	0	7	7	67	9	90	9	73
sec. Butyl N-phenyl carbamate	2	1	0	0	0	0	0	0	0	7	0	12	0	0	0	0	0	0	0	0	0
	8	1	0	0	1	0	0	1	0	2	2	3	5	8	70	6	63	9	92	7	50
	16	9	83	88	9	88	67	8	67	39	7	44	47	9	99	10	100	10	100	10	100
sec. Butyl N-(3-chlorophenyl) carbamate	2	2	0	0	2	0	12	1	0	5	2	8	4	8	77	6	40	7	72	7	77
	8	1	0	0	1	4	0	3	4	13	2	1	17	9	90	9	95	9	92	9	97
	16	9	67	87	8	71	47	7	59	0	7	41	37	9	98	10	100	10	100	9	99
sec. Butyl N-(2-furfuryl) carbamate	2	0	0	0	1	0	13	0	3	8	1	3	0	0	0	0	0	1	10	1	7
	8	0	0	1	0	0	8	1	5	0	1	1	0	1	7	1	13	2	17	0	0
	16	3	33	5	3	17	5	1	16	3	0	13	0	3	45	9	90	1	2	0	0
2-Ethylhexyl N-phenyl carbamate	2	1	3	22	1	9	25	1	8	0	1	1	10	1	10	1	7	1	7	1	7
	8	0	0	13	0	0	0	0	2	0	0	0	0	0	0	0	0	0	0	0	0
	16	9	88	99	9	75	75	3	28	0	4	25	17	1	3	8	95	3	20	0	0
Lauryl N-phenyl carbamate	2	1	0	4	0	0	0	1	0	20	2	10	13	0	0	0	0	1	3	0	0
	8	0	0	0	0	0	0	0	4	11	0	6	0	0	0	0	0	0	0	0	0
	16	9	88	96	9	90	82	8	40	10	4	23	15	1	7	9	97	2	10	0	0
Benzyl N-phenyl carbamate	2	0	0	0	3	0	0	0	0	5	0	0	0	0	0	0	0	0	0	0	0
	8	1	0	0	0	0	0	2	0	7	3	8	10	0	0	0	0	2	13	1	3
	16	0	8	98	3	17	0	0	5	0	2	6	0	0	0	0	0	0	0	0	0
sec-Butyl 2-methylphenyl carbonate	2	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
	8	1	0	20	1	12	0	1	10	16	2	0	25	2	17	0	0	0	0	0	0
	16	0	0	0	0	0	0	0	1	0	0	0	0	0	0	0	0	0	0	0	0
3-Chloroacetanilide	2	0	0	0	0	0	0	1	10	7	0	19	0	0	0	0	0	0	0	0	0
	8	0	0	0	0	0	0	0	0	11	0	5	0	0	0	0	0	0	0	0	0
	16	3	17	18	7	7	2	1	10	0	1	13	3	7	63	9	92	5	17	0	0
Acetoacelanilide	2	0	0	0	0	0	0	0	0	2	0	0	0	0	3	0	0	0	0	0	0
	8	0	0	10	1	1	8	0	0	0	0	0	0	1	7	0	0	0	0	0	0
	16	0	0	17	0	6	5	0	0	0	0	0	0	0	0	0	0	0	0	0	0
Isobutyranilide	2	0	0	3	0	4	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
	8	0	0	0	0	0	0	0	1	0	0	0	0	0	0	0	0	0	0	0	0
	16	0	0	14	1	0	5	0	0	0	0	0	0	3	23	4	55	0	0	0	0
3-Chloroisobutyranilide	2	0	0	3	0	0	0	0	0	0	0	1	0	1	10	1	10	0	0	0	0
	8	1	0	9	0	4	0	0	1	0	0	0	0	1	30	6	62	1	0	1	7
	16	0	0	10	0	14	8	0	2	0	1	0	7	4	55	6	62	3	28	1	10
Ethyl 2-methylindole-3-acetate	2	0	0	1	0	0	0	0	0	0	0	3	0	2	33	0	0	0	0	0	0
	8	0	0	4	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
	16	0	0	7	1	5	0	0	0	0	1	0	7	0	0	0	0	1	7	0	0

Table 1—(Concluded)

Chemical name	Rate per A lbs.	Crops												Weeds							
		Cotton			Soybeans			Corn			Wheat			Mustard		Pigweed		Ryegrass		Crabgrass	
		Inj. rat. No.	Ht. red. Pct.	Plt. k. Pct.	Inj. rat. No.	Ht. red. Pct.	Plt. k. Pct.	Inj. rat. No.	Ht. red. Pct.	Plt. k. Pct.	Inj. rat. No.	Ht. red. Pct.	Plt. k. Pct.	Inj. rat. No.	Plt. k. Pct.	Inj. rat. No.	Plt. k Pct.	Inj. rat. No.	Plt. k. Pct.	Inj. rat. No.	Plt. k. Pct.
N-(3-chlorophenyl)-N′-isopropyl urea	2	1	2	18	1	4	5	0	1	0	1	0	3	0	3	0	0	0	0	0	0
	8	0	0	15	1	0	0	0	0	0	1	0	17	3	32	0	0	2	17	2	3
	16	1	4	23	1	4	0	1	13	8	3	4	30	3	32	2	17	4	35	2	7
N-Carboisopropoxy-phthalimide	2	0	0	10	0	0	5	0	0	5	0	0	0	0	0	0	0	0	0	0	0
	8	0	0	10	0	0	0	0	0	0	0	0	0	1	7	1	7	0	0	0	0
	16	0	0	3	0	0	0	0	0	0	0	0	0	5	53	2	30	0	0	1	7
Amino triazole[11]	2	1	0	13	1	0	0	1	5	0	2	1	13	4	27	3	22	2	17	2	17
	8	2	0	6	2	9	4	2	2	11	5	9	20	6	87	5	70	5	52	6	60
	16	1	0	1	2	5	17	0	8	0	3	0	0	8	78	5	50	5	40	7	60
Alkanolamine salt of 2,4-D[7]	1	2	4	0	3	27	5	3	16	0	2	10	2	4	47	9	95	9	95	7	40
3-p-chlorophenyl-1,1-dimethylurea[8]	2	1	8	0	1	12	0	1	3	0	0	6	3	7	88	9	99	7	80	2	80
Dichloral urea[9]	16	0	0	0	1	15	0	1	5	0	0	0	0	9	99	9	95	9	93	1	3
Alkanolamine salt of dinitro ortho secondary butylphenol[10]	2	1	2	30	1	11	0	0	0	0	0	0	13	9	97	6	61	5	33	2	13
	8	0	0	26	0	0	2	0	0	0	1	0	17	10	100	10	100	9	93	9	93
	16	1	0	3	2	21	0	3	8	2	4	3	40	10	100	10	100	10	100	9	97

[1]IPC—experimental sample supplied by U. S. Industrial Chemicals Company, Baltimore, Md.
[2]CIPC—chemically pure sample supplied by USI.
[3]CIPC—pilot batch sample supplied by USI.
[4]CIPC—commercial formulation supplied by Columbia Southern Chemical Company.
[5]Isopropyl N-(4-chlorophenyl) carbamate—chemically pure sample supplied by Columbia Southern Chemical Company.
[6]Isopropyl N-(4-chlorophenyl) carbamate—chemically pure sample supplied by USI.
[7], [10]Experimental samples supplied by the Dow Chemical Company.
[8]Experimental sample supplied by E. I. du Pont deNemours & Company.
[9]Experimental sample supplied by Carbide and Carbon Chemicals Company.
[11]Experimental sample supplied by the American Chemical Paint Company.
[12]Experimental sample supplied by Spencer Chemical Company.
[*]Inj. rat. No.—Injury rating: 0—no effect; 10—complete kill.
Ht. red. Pct.—Percentage height reduction as compared to a check.
Plt. k. Pct.—Percentage plants killed as compared to a check.

Chlorophyll Inhibition.

These studies confirm earlier work which has shown that the carbamates are considerably more active when applied to the soil in close proximity to the seed or young seedlings than when applied as post-emergence foliage treatments. However, these experiments have indicated a type of response not previously reported. In addition to the systemic and inhibitory effects produced by certain carbamate derivatives, several of the compounds listed in Tables 1 and 2 have inhibited chlorophyll synthesis in crabgrass, ryegrass, corn and to a lesser extent in mustard, and pigweed. These results are of considerable interest since pigweed, ragweed *(Ambrosia artemisiifolia)* and other annual broadleaved weeds have appeared quite tolerant to IPC and CIPC under field conditions. It has also been observed that CIPC may often inhibit the growth of crabgrass and other grasses without killing the plants.

Isopropyl N-(3-chloro-6-methylphenyl)carbamate [isopropyl N-(2-methyl-5-chlorophenyl)carbamate], isopropyl N-(3-chloro-6-methoxyphenyl)carbamate [isopropyl N-(2-methoxy-5-chlorophenyl)carbamate], isopropyl N-(3-trifluoromethylphenyl)carbamate, and isopropyl N-(3-methylphenyl)carbamate in order of decreasing intensity have inhibited chlorophyll synthesis in crabgrass, ryegrass, corn, mustard and pigweed in addition to the systemic and inhibitory effects induced by IPC and CIPC. These chemicals did not affect chlorophyll synthesis in cotton and soybeans. The property of the carbamates to inhibit chlorophyll production in plants does not appear to be associated with total activity. Isopropyl N-(3-methylphenyl)carbamate was more active but less effective in inhibiting chlorophyll synthesis than most of the compounds which induced these effects. All of the chemicals that inhibited chlorophyll production showed less total activity than CIPC. These results suggest that the inhibition of chlorophyll synthesis by the carbamates is associated with the substitution of methyl, methoxy and/or chloro groups or combinations of these groups on the 3 or 3 and 6 positions on the benzene ring. Further studies are in progress to study combinations of methyl, chlorine, and other substitutions on the benzene ring in order to obtain the total activity exhibited by isopropyl N-(3-chlorophenyl)-carbamate and also to maintain the property of inhibiting chlorophyll production.

Selectivity and Specificity.

The degree of selectivity and specificity exhibited by the various carbamates is indicated in Table 1. It is readily evident that generalizations concerning the specificity of the carbamates as a group of compounds is not possible. A review of the data in Table 1 indicates that some derivatives killed both of the broadleaf weed species and both of the grass species. Other derivatives appeared to be toxic to the broadleaved weeds but not to the grasses, while with still others, the results were just the opposite. It may also be noted that several of the chemicals were more injurious to crabgrass than ryegrass and that others were more toxic to ryegrass than crabgrass. Some of the

derivatives were also more effective in killing mustard than pigweed while others were more effective in killing pigweed than mustard.

It may be noticed in Table 1 that *sec.* butyl N-(3-chlorophenyl)-carbamate, isopropyl N-(3-methylphenyl)carbamate, isopropyl N-(3-chlorophenyl)carbamate and several other derivatives effectively controlled both the broadleaved weeds and grasses. It is evident also that isopropyl N-plenylcarbamate was largely ineffective in controlling crabgrass as compared to the compounds discussed above. It is of considerable significance that isopropyl N-(2-methylphenyl)carbamate and several other derivatives were effective in controlling ryegrass with little or no effect on the crop plants, broadleaved weeds, or crabgrass. Isopropyl N-(3,4-dichlorophenyl)carbamate appeared to be effective in controlling pigweed with little or no effect on mustard. Under similar conditions, *n*-butyl N-phenylcarbamate appeared to be highly effective in controlling pigweed and mustard with little or no effect on ryegrass and crabgrass. These examples indicate the high degree of specificity among the carbamates lisited in Table 1. These results also strongly suggest the need for evaluating mixtures of several of these derivatives in order to obtain a compound that will control crabgrass and other annual grasses and in addition control certain broadleaf weeds, such as ragweed which appears quite tolerant to isopropyl N-(3-chlorophenyl)carbamate.

Volatility, Vapor Activity and Persistence In the Soil.

Observations made during these investigations both in the greenhouse and under field conditions indicate clearly that isopropyl N-phenylcarbamate, isopropyl N-(3-chlorophenyl)carbamate, isopropyl N-(3-methylphenyl)carbamate, *sec.* butyl N-(3-chlorophenyl)-carbamate and others are volatile and that the vapors from these chemicals possess herbicidal activity. The eight test plants in untreated flats in the greenhouse were placed adjacent to flats treated pre-emergence with the derivatives indicated above. The above ground parts of ryegrass, crabgrass, wheat and corn showed marked response from the vapors while cotton, soybeans, pigweed and mustard showed little or no response. In further studies under field conditions using 30 test plants, vapor activity from the compounds above on untreated adjacent test plants was again observed. The vapors of the chemicals studied had no detectable affect on test plants that were as much as ten feet from the treated plots. It would appear from these preliminary observations that vapors from the carbamates listed in Table 1 would not produce a practical hazard to untreated crops near treated areas under field conditions.

Other workers (2) have indicated significant differences in the rate of evaporation of several carbamates. The present studies and others (2) would indicate that the loss of a volatile carbamate through evaporation might cause a reduction in its initial as well as its residual herbicidal activity. It seems possible that under conditions of very high soil temperatures (90° to 100°F) the herbicidal rate of a volatile carbamate applied to the soil pre-emergence could be reduced to a non-herbicidal rate through loss of the chemical by volatilization

prior to emergence of the crops and weeds resulting in unsatisfactory weed control.

Preliminary studies have been conducted under greenhouse conditions on the persistence of the herbicidal activity in the soil of the twenty most active compounds in Table 2. These investigations indicate that persistence of the herbicidal effects of the carbamates in the soil is correlated with their level of herbicidal activity. The derivatives with the highest phytotoxicity ratings in Table 2 have had the longest residual activity in the soil. The esters of carbamic acid are known to possess vapor pressure. The present preliminary studies suggest that evaporation of the carbamates may greatly affect their performance as pre-emergence herbicides.

Much additional research is needed to more thoroughly evaluate the relationships among volatility, vapor activity, and persistence of the carbamates in the soil.

Herbicidal Activity.

The relative activity of the various carbamate derivatives is shown in Table 2. The phytotoxicity rating of a chemical in Table 2 is obtained by adding all of the values obtained for each chemical rate and for each plant species in Table 1. The injury rating, the percentage height reduction, and the percentage plant kill values are all added and this value is reported in Table 2 as the phytotoxicity rating. It may be noted that no percentage height reduction value for the weed species is included in Table 1 and therefore, activity on the crops is weighted somewhat more heavily than on the weeds in the phytotoxicity rating value. Since this is a differentially weighted value, care must be exercised in interpretation. The compounds in Table 2 have been ranked in descending order of total activity as determined by the phytotoxicity rating value. Since part of the phytotoxicity rating value contains an estimate, a degree of accuracy in ranking the compounds may be implied which may not be real. For this reason, the compounds in Table 2 should be interpreted as belonging in four groups of activity as follows: (1) very active, (2) moderately active, (3) slightly active and (4) minor activity to inactive. This activity classification is reported in Table 2 to aid in interpreting the phytotoxicity rating value. The phytotoxicity rating value is useful only in giving some indication of the relative difference in the degree of activity of compounds placed in the various activity classification groups. In studying the data in Tables 1 and 2, it is obvious that a particular compound may have a low phytotoxicity rating in Table 2 and yet show activity on one or more plant species in Table 1.

Relationship Between Structure and Herbicidal Activity.

The data in Tables 1 and 2 suggest a high degree of correlation between structural configuration and herbicidal activity in the N-phenyl and substituted N-phenylcarbamates. The greatest activity of the derivatives studied seems associated with the isopropyl and secondary butyl derivatives of both the N-phenyl and substituted

Table 2—The relation of molecular configuration of several carbamates to herbicidal activity.

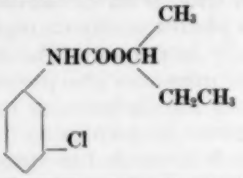
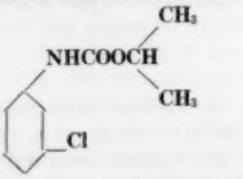
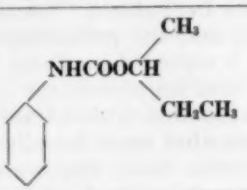
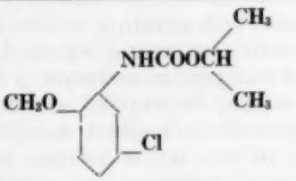
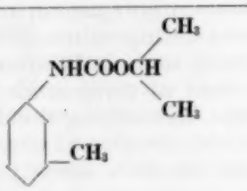
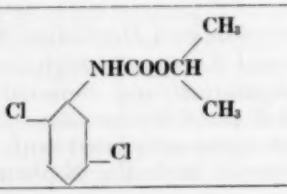
Chemical	Structure	Phytotoxicity rating	Activity classification
sec. Butyl N-(3-chlorophenyl) carbamate		1660	Very active
Isopropyl N-(3-chlorophenyl) carbamate		1520	Very active
sec. Butyl N-phenylcarbamate		1330	Very active
Isopropyl N-(3-chloro-6-methoxyphenyl) carbamate		1280	Very active
Isopropyl N-(3-methylphenyl) carbamate		1180	Very active
Isopropyl N-(3,6-dichlorophenyl) carbamate		1180	Very active

Table 2—(Continued)

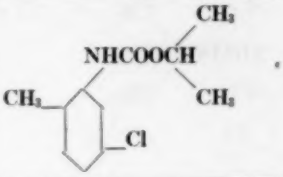
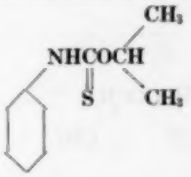
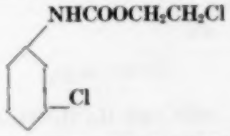
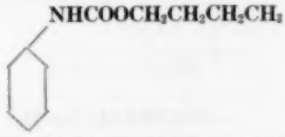
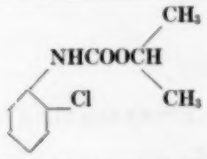
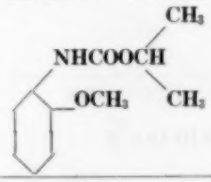
Chemical	Structure	Phytotoxicity rating	Activity classification
Isopropyl N-(3-chloro-6-methylphenyl) carbamate		1100	Very active
Isopropyl N-phenylthionocarbamate		1060	Very active
2-Chloroethyl N-(3-chlorophenyl) carbamate		1030	Very active
n-Butyl N-phenylcarbamate		1000	Very active
Isopropyl N-(2-chlorophenyl) carbamate		990	Moderately active
Isopropyl N-(2-methoxyphenyl) carbamate		810	Moderately active

Table 2—(Continued)

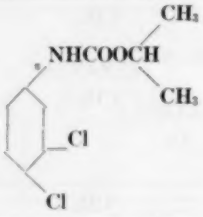
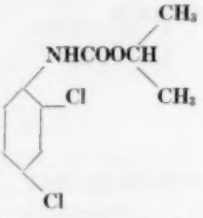
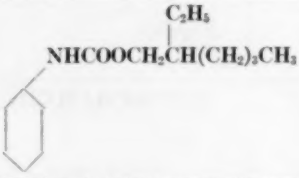
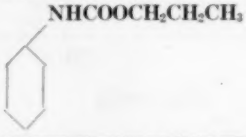
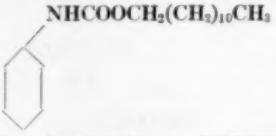
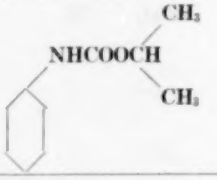
Chemical	Structure	Phytotoxicity rating	Activity classification
Isopropyl N-(3,4-dichlorophenyl) carbamate		770	Moderately active
Isopropyl N-(2,4-dichlorophenyl) carbamate		730	Moderately active
2-Ethylhexyl N-phenylcarbamate		690	Moderately active
n-Propyl N-phenylcarbamate		690	Moderately active
Lauryl N-phenylcarbamate		680	Moderately active
Isopropyl N-phenylcarbamate		660	Moderately active

Table 2—(Continued)

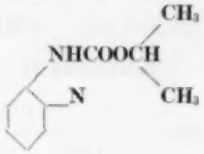
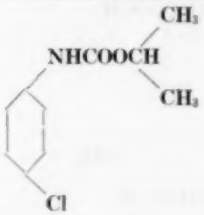
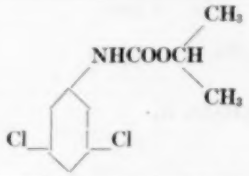
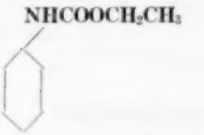
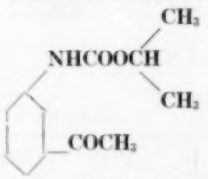
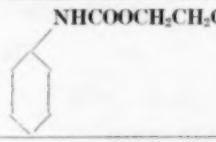
Chemical	Structure	Phytotoxicity rating	Activity classification
Isopropyl N-(2-pyridyl) carbamate		630	Moderately active
Isopropyl N-(4-chlorophenyl) carbamate		600	Moderately active
Isopropyl N-(3,5-dichlorophenyl) carbamate		570	Moderately active
Ethyl N-phenylcarbamate		520	Moderately active
Isopropyl N-(3-acetophenyl) carbamate		390	Slightly active
3-Chloropropyl N-phenylcarbamate		370	Slightly active

Table 2—(Continued)

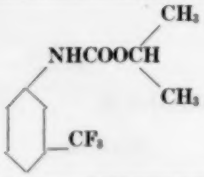
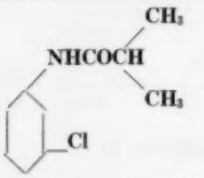
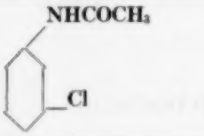
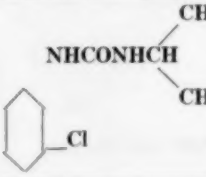
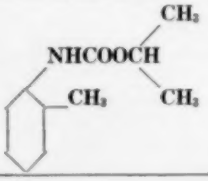
Chemical	Structure	Phytotoxicity rating	Activity classification
sec. Butyl N-(2-furfuryl) carbamate		350	Slightly active
Isopropyl N-(3-trifluoromethylphenyl)-carbamate		350	Slightly active
3-Chloroisobutyranilide		350	Slightly active
3-Chloroacetanilide		330	Slightly active
N-(3-chlorophenyl) -N-isopropyl urea		330	Slightly active
Isopropyl N-(2-furfuryl) carbamate		310	Slightly active
Isopropyl N-(2-methylphenyl) carbamate		230	Slightly active

Table 2—(Continued)

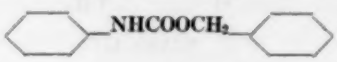
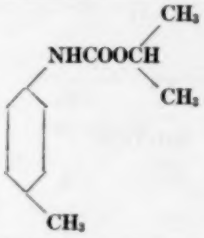
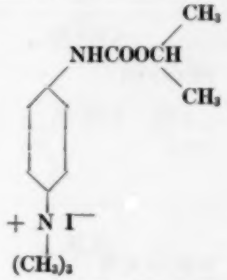
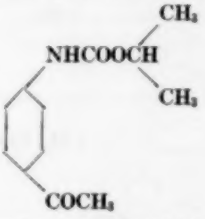
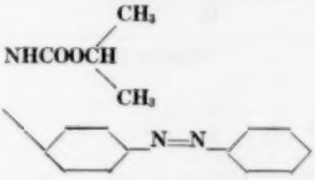
Chemical	Structure	Phytotoxicity rating	Activity classification
Benzyl N-phenylcarbamate		200	Slightly active
Isopropyl N-(4-methylphenyl) carbamate		190	Minor activity
Isopropyl N-(4-dimethylamino phenyl)-carbamate methiodide		180	Minor activity
Isopropyl N-(4-acetophenyl) carbamate		170	Minor activity
Isopropyl N-(4-phenylazophenyl) carbamate		160	Minor activity

Table 2—(Continued)

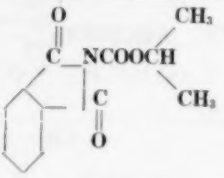
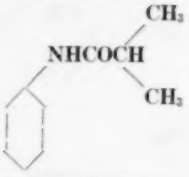
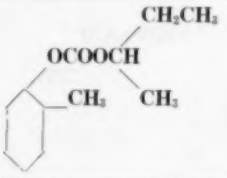
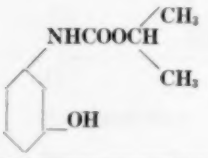
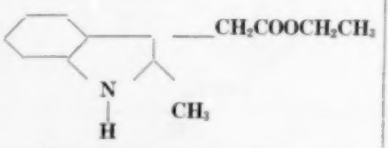
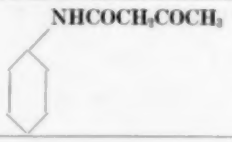
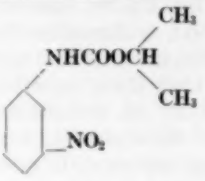
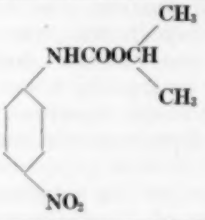
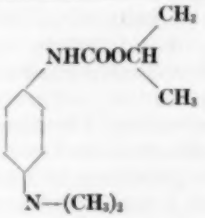
Chemical	Structure	Phytotoxicity rating	Activity classification
N-Carboisopropoxyphthalimide		150	Minor activity
Isobutyranilide		110	Minor activity
see. Butyl 2-methylphenylcarbonate		110	Minor activity
Isopropyl N-(3-hydroxyphenyl) carbamate		80	Minor activity
Ethyl 2-methylindole-3-acetate		70	Minor activity
Acetoacetanilide		60	Minor activity

Table 2—(Concluded)

Chemical	Structure	Phytotoxicity rating	Activity classification
Isopropyl N-(3-nitrophenyl) carbamate		——	Moderately active
Isopropyl N-(4-nitrophenyl) carbamate		——	Slightly active
Isopropyl N-(4-dimethylaminophenyl) carbamate		——	Minor activity

N-phenylcarbamates. While the greatest activity appears to be in these two derivatives, the data in Tables 1 and 2 indicate clearly that other derivatives such as 2-chloroethyl, *n*-butyl, 2-ethylhexyl, propyl, lauryl, and ethyl possess activity. The data also indicate that within the isopropyl series and the group of mono substituted N-phenylcarbamates reported in this study, substitution in the 3-position whether it be chloro, methyl, trifluoromethyl, nitro, aceto, hydroxy or other groups produces the greatest activity. However, it is obvious from the data in Table 2 that these substituted groups do not contribute equally to the activity of the derivative resulting from the substitution. The results of these studies suggest the following order on the basis of decreasing activity: chloro, methyl, methoxy, trifluoromethyl, nitro, aceto, and hydroxy. It should be pointed out that substitution in the 3-position does not insure activity. Substitution of a hydroxy group in the 3-position produced little or no activity. These data also indicate that active compounds result from substitution in the 2-position but that very little activity is obtained by substitution in the 4-position. When substitutions are made in the 2-position or 4-position the activity contributed by the substituted groups studied in these experiments remains in the same relative order as discussed above for substitution in the 3-position.

Activity within the group of di-substituted N-phenylcarbamates is of interest. The property of inhibiting chlorophyll production in crabgrass and other plants, in addition to the relatively high activity of isopropyl N-(3-chloro-6-methyl)carbamate and isopropyl N-(3-chloro-6-methoxyphenyl)carbamate suggests the need for further study of closely related derivatives. The results of these experiments with the isopropyl series indicate that substitution in the 3 and 6 positions (2 and 5) produces the greatest activity followed by substitution in the 3 and 4, 2 and 4, and 3 and 5 positions in order of decreasing activity in the di-substituted N-phenyl-carbamates. Substitution in the 3 and 6 positions produces less total activity than mono substitution in the 3-position but the property of inhibiting chlorophyll production is increased. Further studies are needed to establish the order of activity of the substituted groups in the di-substituted N-phenylcarbamates. The data in Tables 1 and 2 indicate that substitution of combinations of unlike groups such as methyl and methoxy with chloro groups in the 3 and 6 positions produces activity equal to and chlorophyll inhibition greater than that obtained by the substitution of two chloro groups in the same positions.

Plant breeders have demonstrated that the production of certain pigments in plants or the failure to produce chlorophyll in plants is associated with genes carried on certain chromosomes and that the character of albinism in plants is a simple recessive to normal green (4). As early as 1939 it was shown (13) that phenylurethanes and colchicine had similar actions on plant cells. In 1949 further work (7) indicated that certain aryl carbamic esters produced striking cytological aberrations in certain plant species. A proposed explanation of the mechanism involved in chlorophyll inhibition by certain carbamates in several plant species may be that chromosome aberra-

tions occur involving genes which control the production of chlorophyll in plants.

In interpreting the results reported in Table 1, it should be pointed out that the relatively low activity of the various carbamates on corn and wheat is due primarily to the mechanical protection afforded by depth of planting rather than plant tolerance. Since no water is added to the soil surface, there is minimum vertical movement of the chemical in the soil and only the terminal shoot tissue of the crop plants comes in contact with the chemical. The weeds, however, are planted near the surface (¼ inch deep) and therefore the seeds, roots, and stems of the weeds are in close proximity to the chemical at the time of and after germination. When the chemicals were thoroughly mixed with the soil for persistence studies, all crop plants were killed except cotton and soybeans. These studies indicate clearly that the tolerance of corn and wheat to the most active group of carbamates is due primarily to mechanical protection afforded by depth of planting, chemical placement and minimum chemical movement in the soil. However, cotton and to a considerably lesser extent soybeans show some tolerance to the carbamates regardless of the above factors.

Isopropyl N-phenylcarbamate was one of the most variable compounds evaluated. This compound and isopropyl N-(3-chlorophenyl)-carbamate have been included as standards in every experiment conducted. Under greenhouse conditions, chemically pure IPC from the same experimental sample has received phytotoxicity ratings ranging from 700 to 1500. The phytotoxicity ratings for CIPC and the other carbamates in Table 2 with a very active rating have shown very low variability in repeated tests. For example, the phytotoxicity rating value for CIPC has varied from 1300 to 1500 and the rating for isopropyl N-(3-chloro-6-methylphenyl)carbamate has varied from 1100 to 1300. The variable performance of IPC under field conditions has been reported by numerous workers. Others (2) have indicated that evaporation may account for the rapid loss of IPC from sprayed surfaces. This phenomenon may account for some of the variability in the performance of IPC applied as a pre-emergence spray.

Some of the carbamate derivatives, especially isopropyl N-(3-methylphenyl)carbamate appeared to show distinct formulation advantages when compared to IPC. Chemically pure isopropyl N-(3-methylphenyl)carbamate is a liquid that is highly soluble in acetone, xylene and other organic solvents. The chemical when dissolved in acetone emulsifies readily when mixed with water. The emulsion formed is sufficiently stable to permit application with minimum agitation.

Field experiments with 29 of the most active compounds in Table 1 involving the application of each chemical as a pre- and post-emergence spray on 30 plant species confirm the results reported herein.*

*These results are available upon request as a processed publication from the authors.

SUMMARY

These preliminary studies with several carbamate derivatives may be summarized as follows:

1. Several carbamate derivatives, including *sec.* butyl N-phenylcarbamate, isopropyl N-(3-chloro-6-methylphenyl)carbamate, isopropyl N-(3-chloro-6-methoxyphenyl)carbamate, isopropyl N-(3-methylphenyl)carbamate, isopropyl N-(3,6-dichlorophenyl)carbamate and others in addition to isopropyl N-(3-chlorophenyl)carbamate and isopropyl N-phenylcarbamate have exhibited a high degree of herbicidal activity.

2. Isopropyl N-(3-chloro-6-methylphenyl)carbamate, isopropyl N-(3-chloro-6-methoxyphenyl)carbamate, isopropyl N-(3-trifluoromethylphenyl)carbamate, and isopropyl N-(3-methylphenyl)carbamate have inhibited chlorophyll production in several plant species, especially crabgrass, resulting in complete kill of the plant. This mode of action appears to be highly correlated with the substitution of methyl, methoxy and similar groups with or without chloro groups in the 3 and 6 positions on the benzene ring.

3. These studies indicate a high degree of correlation between molecular configuration and herbicidal activity.

4. Several of the carbamate derivatives appear to be volatile and this property may be important in determining the possible length of residual weed control and also residual toxicity in the soil.

5. A proposed explanation of the mechanism involved in chlorophyll inhibition by certain carbamates in several plant species, may be that chromosome aberrations occur involving genes which control the production of chlorophyll in plants.

6. A high degree of selectivity and specificity has been exhibited by the various carbamates studied in these experiments.

7. Results obtained from field experiments in which 29 of the most active carbamates were applied as pre- and post-emergence sprays on 30 plant species confirmed the results reported herein.

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Comments: On Quack Grass Control with Maleic Hydrazide

OTTO L. HOFFMAN and E. P. SYLWESTER

QUACK GRASS, *Agropyron repens,* has not been controlled where maleic hydrazide (MH) has been applied without any further treatments (1, 2, 3, 4, 5). Friesen (4) did obtain a high percentage of control with 16 pounds MH per acre. However, other investigators did not obtain this degree of control.

The nearly perfect control of *Polygonum coccineum* with MH applications followed by cutting at the ground level or spraying the tops with a contact herbicide (5) indicated that this method might be applicable for quack grass control.

Areas of quack grass 10 feet by 20 feet were sprayed with MH at 4 and 8 pounds per acre. The sprayed areas were divided into 5 by 5 foot plots for further treatment. Some of the plots were turned over with a spading fork and some of the plots were defoliated with a dinitro spray in oil. These further treatments indicated in table 1 were carried out on three dates: the same day, eleven days after, and 20 days after the MH was applied. All growing weeds were cut with a scythe in September. The plots with the 0 rate of MH application were not included in the main split plot design but were in separate plots adjoining the main plot. Quack grass in an adjacent garden plot was not controlled by normal cultivation. Estimates of stand were taken separately by two investigators. Data on control were obtained on April 23, 1952, and are recorded in table 1.

Table 1. Percent control of quack grass with maleic hydrazide (MH) application on May 4, 1951 followed by digging or spraying with dinitro (DN) in oil.

Treatment after MH application	Rate of MH in pounds per acre						
	0	8			4		
		Rep. 1	Rep. 2	Rep. 3	Rep. 1	Rep. 2	Rep. 3
0	0	0	60	90	0	0	30
0	0	0	0	0	0	10	0
Dug May 4, 1951	20	90	95	99	75	80	90
Dug May 15, 1951	20	99	95	95	90	85	85
Dug May 24, 1951	50	90	98	97	80	80	85
DN Spray May 4, 1951	0	0	0	0	0	0	0
DN Spray May 15, 1951	0	0	30	75	20	0	0
DN Spray May 21, 1951	0	0	20	80	60	0	0

The vigor of the quack grass was reduced in all plots sprayed with MH except in those where the quack was killed back with a dinitro spray immediately after the MH was applied. Since MH has very little toxic action once it is in contact with the soil, it would appear that MH applied at a rate of 8 pounds per acre before plowing for corn or soybeans may give adequate control of quack grass. This

possibility is under investigation at the present time.

CONCLUSIONS

1. MH application at the rate of 8 pounds per acre followed by spading gave 95 percent control of quack grass. The 83 percent control of quack grass with 4 pounds MH per acre followed by spading may be adequate for crop production.

2. There was no difference in the degree of control obtained at the various dates of spading following the MH applications. On the basis of penetration studies it would probably be best to wait for at least two days after MH application before the ground is plowed.

3. MH applications at a rate of 4 pounds or 8 pounds per acre without additional treatment did not control quack grass.

4. Top killing of quack with dinitro sprays after MH application did not enhance the effect of the MH.

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Prepared By

Division of Weed Investigations, Bureau of Plant Industry, Soils, and Agricultural Engineering, Agricultural Research Administration, United States Department of Agriculture

This bibliography of current literature on weeds and their control is issued as a service to those engaged in weed research in the United States and other countries. In issuing this bibliography the Division of Weed Investigations does not assume responsibility for the subject matter cited.

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Prepared By

Division of Weed Investigations, Bureau of Plant Industry, Soils, and Agricultural Engineering, Agricultural Research Administration, United States Department of Agriculture

This bibliography of current literature on weeds and their control is issued as a service to those engaged in weed research in the United States and other countries. In issuing this bibliography the Division of Weed Investigations does not assume responsibility for the subject matter cited.

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